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THE USE

OF

COAL TAR COLORS

IN

FOOD PRODUCTS

BY

HUGO LIEBER

New York
H. LIEBER & CO.
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INDEX.

Preface	5
What are Coal Tar Colors	7
Use of Coal Tar Colors	10
Foreign Pure Food or Sanitary Laws:	
England	11
Austria	12
Germany	16
Italy	17
France	24
Dinitrosoresorcin	35
Naphthol Green B	38
Picric Acid	42
Saffronsurrogate (Dinitrokresol)	46
Martius Yellow	67
Naphthol Yellow S	74
Brilliant Yellow	78
Aurantia	81
Summary	82
Bismarck Brown	84
Sudan I	87
Metanitrazotin	89
Paranitrazotin	90
Orange II	91
Poncean 4 G. B	95
Orseille Substitute	96
Chrysoidin	99
Diphenylamin Orange	102

4 COAL TAR COLORS IN FOOD PRODUCTS.

Metanil Yellow
Azarin S
Fast Brown G
Wool Black
Naphthol Black P
Congo
Azo Blue
Chrysamin R
Conclusions
Cartrazine
Ourcumin
Carmoisin
Ponceau 2 R
Rhodamin B
Naphthol Yellow S
Acid Green S F
Soluble Blue
Naphthol Red S

PREFACE.

For some time there has been considerable agitation against the use of Coal Tar Colors in Food Products, and almost every State in the Union has created what is called a Pure Food Law.

As I am decidedly of the opinion that the food consuming public should be most thoroughly protected by proper laws and their strict enforcement, I at the same time think that these laws should be created by conscientious co-operation of theoretically skilled professional men and such men who have a thorough knowledge of their respective branches of the food industries. Thus alone can be created laws which will yield a perfect protection to the food consuming public, which is the paramount issue, beyond a doubt, but at the same time laws which will give the honest and honorable manufacturer of Food Products a chance to supply the needs of the food consuming public.

"There is a distinction but no opposition between theory and practice; each to a certain extent supposes the other; theory is dependent on practice, practice must have preceded theory."

—SIR W. HAMILTON.

One of the many arguments forwarded by those who advocate the forbidding of the use of any coloring matter in food products is that the food consuming public is deceived. The so-called deception is not a detrimental one, but just the contrary, for it is a well established fact that the digestion is decidedly aided by the desire to eat, and the desire to eat again is decidedly influenced by the appearance of the food presented. Almost all the civilized countries of the Universe have created Sanitary or Pure Food Laws which

are strictly enforced. These laws have been made not for the protection of the food industries or for the protection of color manufacturers, etc., but for the protection of the food consuming public. These laws have proven through the course of years and through practical experience sound laws, "and none of these laws forbids sweepingly the use of coal tar colors, but simply limits their use to such colors which have been proven beyond a question of a doubt to be harmless." I wish to refer to the German, the Austrian, the French, etc., Sanitary Laws.

The time that every housewife could produce her own necessities of life has passed. The great masses have to be fed by the large growers and manufacturers of food products and these food products should necessarily be prepared so as not to be detrimental to the health of the consumer. They must also be prepared so as to offer a pleasing and appetizing appearance, which is again a necessity of a proper food product.

What we need is a law which will plainly state what is forbidden and what is permitted to be used, and then have this law enforced to the very letter. Hypocritical laws can only be detrimental to the consumer as well as to the manufacturer.

This book is not intended to be a scientific treatise of coal tar products, as they are well known to every chemist. My intention is to write a book which will aid the food manufacturers in general to a clearer knowledge of these indispensable ingredients and their relative advantages and disadvantages.

WHAT ARE COAL TAR COLORS?

As the name indicates, coal tar colors are manufactured from coal tar through certain well known processes, which can best be classed as follows:

Distillation of Coal Tar.

Manufacture of Aniline.

Manufacture of the colors.

The coal tar which is furnished by the coal gas manufacturers (by-product) is subject to a dry distillation. The thereby escaping vapors are fractionated and condensed into three main groups as follows:

70—180° C. = Crude Benzol. 180—250° C. = Crude Naphthalin. 250—400° C. = Crude Anthracene.

Through further separation and purification of the above crude products we obtain what may be termed the raw materials for the manufacture of coal tar colors. The most important of these are: Naphthalin, Phenol, Kresol, Toluol, Benzol, Xylol, Anthracene, etc.

By subjecting these raw materials to certain treatments we obtain what is termed intermediate products. For instance, the raw material benzol, when treated with nitric acid, yields the intermediate product "Nitrobenzol," etc. If Nitrobenzol is treated with Iron and Hydrochloric Acid we obtain "Aniline." Aniline when properly treated with Methylic

Alcohol yields "Dimethylanilin," which is largely used in the production of Methylblue, Methylviolet, etc. This shows how the color is produced from the intermediate product. Frequently the intermediate product is first turned into a new product by certain treatment, then this new product is again subject to one or more chemical treatments and then yields the color proper.

For instance: By a certain treatment toluol is turned into a muriate of amidoazotoluol, which again is treated with fuming sulphuric acid.

$$N=N$$
 $N=N$
 $N=N$

This yields the well known color Fast Yellow R. It would lead entirely too far to thus describe the many combinations and colors formed, nor is that the object of this book.

The colors obtained are divided into various groups or classes based upon the relative grouping of the atom in the color molecule.

The main groups are as follows:*

Nitro Colors.

Azoxy Colors.

^{*} G. Schultz & P. Julius. Tabellarische Uebersicht.

Diazoamido Colors.

Azo Colors.

Auramin Colors.

Triphenylmethan—and Diphenylnaphtylmethan—Colors.

Pyronin Colors.

Acridin Colors.

Nitroso Colors.

Oxyketon Colors.

Indophenyl Colors.

Oxazin & Thiazin Colors.

Azine Colors.

Thiobenzenyl Colors.

Chinolin Colors.

Colors of the Indigo group.

Sulphur Colors, etc.

The names under which the various colors are known, that is, their mercantile names, are voluntarily chosen; frequently they are produced by the abbreviation of the scientific names of the respective colors which sometimes are of an enormous length, for instance: The scientific name for Naphthol Blue B is Dimethylamidophenodimethylamido-naphtoxazoni-umchloride.

The names, however, are not to be considered as a guarantee of quality, etc., of a color, as frequently the same names are used for greatly varying products, for instance: Phloxin produced by one manufacturer is the potassium salt of tetrabromdichlor-fluorescein (C_{20} H_4 Cl_2 Br_4 O_5 K_2). It is a brownish yellow powder, soluble in water producing a cherry red solution which has a greenish yellow fluorescence.

Phloxin produced by another manufacturer is the sodium salt of tetrabromtetrachlorfluorescein (C_{20} H_2 Cl_4 Br_4 O_5 Na_2). It is a scarlet powder soluble in water, producing a bluish red solution which has a dark green fluorescence.

USE OF COAL TAR COLORS.

The greatest use of coal tar colors is for dyeing purposes, and the demand for such purposes is a tremendous one, as almost all materials are now colored and dyed with these colors, for instance: Silk, wool, cotton, linen, flax, wood, leather, bones, hair, paper, flowers, feathers, soap, inks, etc. But what is of the most interest to us is the use of these coal tar products for coloring of all kinds of food materials, such as canned and preserved fruits, syrups, catsups, jams, jellies, pastry, candies, wines, cordials, liquors, butter, etc.

Whereas most of the coal tar colors are entirely harmless, there are certain colors and classes which are decidedly detrimental to the human or animal system, and whereas it is less essential, yes, nearly impossible, for every manufacturer of food products to know all those colors which are harmless, it is a matter of absolute necessity for him to know those colors which are detrimental, and which therefore should never be used.

To show how other countries are protecting the food consuming public by forcing the food manufac-

turers to use only such colors which have been proven by thorough experiments to be absolutely harmless, I will quote (translated) those parts of the sanitary laws of the various countries which refer to the use of coloring matters in food products, etc.

ENGLAND.

SALE OF FOOD AND DRUGS ACT, 1875.

Description of Offences.

3. Mixing injurious ingredients with food.—No person shall mix, color, stain, or powder, or order or permit any other person to mix, color, stain, or powder, any article of food with any ingredient or material so as to render the article injurious to health, with intent that the same may be sold in that state, and no person shall sell any such article so mixed, colored, stained, or powdered, under a penalty in each case not exceeding fifty pounds for the first offense; every offense, after a conviction for a first offense, shall be a misdemeanor, for which the person, on conviction, shall be imprisoned for a period not exceeding six months with hard labor.

Sale of Food and Drugs Act, 1899.

7. For the purpose of this section an article of food shall be deemed to be adulterated or impoverished if it has been mixed with any other substance, or if any part of it has been abstracted so as in either case to effect injuriously its quality, substance or nature.

Provided that an article of food shall not be deemed to be adulterated by reason only of the addition of any preservative or coloring matter of such a nature and in such quantity as not to render the article injurious to health (g).

AUSTRIA.

PAR. 408.

The use of mineral colors containing copper, arsenic, lead and zinc is forbidden in the manufacture of food products as well as also for painting of such materials which come in direct contact with the human body.

The use of starch which has an admixture of above mineral colors is also forbidden.

[On the 1st of March, 1886, the Imperial Austrian Government passed a sweeping law forbidding absolutely the use of all coal tar colors in the manufacture of food products. However, the Government was soon convinced of its mistake, and the law was repealed, and a new law substituted for same. Quoting both laws herewith (translated)]:

I. Law of the Minister of State in co-operation with the Ministers of Commerce, Justice and Police, May 1, 1886, concerning the use of poisonous colors

and preparations detrimental to health in the manufacture of various utensils and the sale of same.

- §1. Forbidden is the use of such colors which contain metals (iron excepted), such as gamboge, picric acid, or aniline in the manufacture of food products, including also figures, etc., used for decorating purposes and manufactured from tragacanth, starch and sugar.
- II. Law of the Minister of the Interior in co-operation with the Ministers of Commerce and Justice, March 1, 1886, concerning the use of aniline or coal tar colors in food products.

The use of colors which have been produced by the chemical action upon aniline or other coal tar products, especially of Rosolsaeure, manufactured by various methods, is forbidden in the manufacture of food products of all kinds, in accordance with §§ 1 & 6 der Vdg. vom Mai, 1866.

III. Law of the Ministers of the Interior, Finance, Commerce and Agriculture of August 10, 1892, concerning the forbidding of importation of wines colored with coal tar colors.

The importation of wines colored with coal tar colors into Austria or Hungary is forbidden.

V. Law of the Minister of the Interior in co-operation with the Ministers of Commerce and Justice, September 19, 1895, concerning the use of certain coal tar colors for coloring of cakes, pastries, candies, and such cordials which are colorless, but which, however, through custom, are always colored artificially.

The law created by the Minister of State in co-op-

eration with the Ministers of Commerce, Justice and Police, May 1, 1886, and the law of the Minister of the Interior in co-operation with the Ministers of Commerce and Justice of March 1, 1886, forbidding the use of aniline or coal tar colors in the manufacture of food products, is hereby repealed and cancelled as far as the coloring of cakes, pastries, candies and the customary artificially colored cordials Permitted is the use of Fuchsine, Acid concerned. Fuchsine, Roscellin, Bordeaux, Ponceau, Eosin, Erythrosin, Phloxin, Alizarine Blue, Aniline Blue, Water Blue, Induline, Acid Yellow R., Tropæolin 000 (Orange I), Methylviolett, Malachitgreen, as well as also the green colors produced by mixing of the socalled Blue and Yellow colors.

The above mentioned colors permitted for coloring of cakes, pastries, candies and cordials can be used for such purposes only then, if same have been purchased in the original packages of the manufacturer. The wrapper of the package must contain the statement that this coal tar color is adapted for use in food It must also contain the seal or trade mark of the manufacturer, as well as also the date and certificate of a chemical institute, confirming the purity of the product as well as also that it is free of all deleterious admixtures in accordance with chemical analysis made at least once a year. The manufacturer of colors shall at all times be held responsible that the colors sold by him with the above mentioned guarantees, seals, trade-marks, etc., shall be free of all deleterious adulterations, be same of a metallic or organic nature.

VI. Law of the Minister of the Interior in co-operation with the Ministers of Commerce and Justice, Jan. 22, 1896, concerning additions to the law of September 19, 1895, concerning the use of non-poisonous coal tar colors.

Besides the coal tar colors mentioned in the law of September 19, 1895, it is also permitted to use Naphthol Yellow (sodium salt of Dinitro-a-Naphthol sulphosäure) in coloring of cakes, pastries, candies and cordials.

The scientific names of the other coal tar colors permutted to be used are:

Fuchsine—Rosanilinchlorhydrate.

Acid Fuchsine or Fuchsine S. or Rubine—Acidulous sodium or calcium salt of Rosanilindisulpho acid.

Rocellin or Roscellin—Sulpho-Oxyazonaphtalin.

Bordeaux and Ponceau red—Products of the combination of β -Naphthol-disulpho acid with diazo combinations of Xylol of a higher homologene of benzol.

Eosin—Tetrabrom-Fluorescein.

Erythrosin—Tetrajod-Fluorescein.

Phloxin—Tetrabrom-Dichlor-Fluorescein.

Alizarine Blue—C₁₇H₉NO₄.

Aniline Blue—Triphenilrosanilin.

Water Blue—Sulpho acid of Triphenilrosanilin (soluble Blue).

Induline—Sulpho acid of Azodiphenil Blue and its derivatives.

Acid Yellow R. or Brilliant Yellow R.—Amido Sulpho-azobenzol.

Tropaeolin 000 or Orange I.—Sulphoazobenzol-a Naphthol.

Methylviolet—Hexa and Penta-Methyl-Pararosanilin-chlorhydrate.

Malachit Green — Tetramethyl - Diamidotriphenyl-Carbinol-chlorhydrate.

GERMANY.

ART. III. Law concerning the use of colors detrimental to health in the manufacture of food products and utensils—July 5, 1887:

§ 1. It is forbidden to use colors detrimental to health in the manufacture of food products of any description which are intended for sale.

Colors detrimental to health in the sense of this law are such colors, coloring materials and compositions which contain antimony, arsenic, barium, lead, cadmium, chrome, copper, quicksilver, uranium, zinc, tin, gamboge, corallin and picric acid.

The Reichskanzler is empowered to specify the methods to be used in determining the presence of arsenic and tin.

§ 2. In the manufacture of containers and packages intended for food products which are intended for sale, or their coverings, colors as stated in § 1 must not be used, but in their manufacture may be used sulphate of barium, barium lacquers of carbonate of barium, chrome oxide, the so-called bronze colors containing copper, tin [and zinc, tin oxide, cinnabar and

sulphate of tin as well as all colors burned into the glass or enamels. This exception shall also extend to the exterior coloring of vessels.

§ 3. For the manufacture of cosmetic materials (materials for cleansing or coloring the skin, the hair and the mouth) which are intended for sale, the materials which are mentioned in § 1 shall not be used.

ITALY.

Ample and harmful fraud is employed in coloring food products with detrimental and mineral substances.

The following salts must be forbidden from this use:

Mixtures	of copper	(Colorations	of	azure	or
"	" lead	green). (Colorations	fron	\mathbf{w} hite	to
"	" barium	yellow). (Colorations	of	chro	me
"	" arsenic	yellow). (Colorations	of a	a green	ish
"	" mercury	type). (Colorations	of r	ed Cinı	ıa-
"	" antimony	bar). (Colorations	of :	yellow	or
		red).			

Gamboge (Yellow coloration).

Eosin and derivatives (Yellow-reddish coloration).

Fuchsine and derivatives (Red, Blue and Violet colorations).

The following may be used, however:

Azure Colors—Indigo, azure of Berlin, ultramarine.

Red "—Cochineal, carmine, carmined lac, oricello, Brazilian lac.

Yellow "—Saffron, grain of Avignone, curcuma, etc.

Green "—Mixtures of Indigo or Azure of Berlin with yellow colored matters.

Violet "—Indian wood, mixtures of Indigo or azure of Berlin with red of vegetable nature.

Coal tar products: Bordeaux Red, Chrisoidin, Biebrich Red, Naphthol Yellow S.

Royal Decree No. 55.—Feb. 4th, 1902, Printed in the *Official Gazetta* of the 29th of the same month: Humbert 1st by the Grace of God and the Will of the Nation king of Italy.

LIST OF THE HARMFUL COLORS IN THE ALIMENTARY SUBSTANCES.

Having examined the law for the tutelage of the public health, Dec. 22nd, 1888, No. 5849 (Sect. 3), having examined the clause 130 of the special rule for the hygienic vigilance, for food products, beverages and for articles of domestic use, approved with Royal

decree Aug. 30th, 1890, No. 7045 (Sect. 3), having examined the list of the harmful colors compiled by the Minister of the Interior, according to Article 43 of the aforesaid law and communicated, with circular, July 8th, 1890, to all the Prefects of the kingdom, in order to avoid the danger of misinterpretations and to obtain that the determination of the Salts of Copper in the alimentary conserves, contemplated in the said list, takes place in all the kingdom with equal judgment as well as for the criminal effects; having heard the opinion of the officers of the Board of Health and of the Ministers, upon the proposal of our Secretary of State for the Interior, we have decreed and decree:

ART. 1. The preparations of Salts or Copper contained in the alimentary conserves (see Art. 130) must be calculated in metallic copper, and prohibited are only those conserves which contain more than one-tenth of a gram of metallic copper for each kilo of weight.

ART. 2.—The list of the harmful colors which was modified by our Minister of the Interior, in the last line of the table-A in conformity with the former clause, is the following:

List of harmful colors compiled by our Minister of the Interior in accordance with clause 43 of the law regarding the public health.

Harmful colors which must not be used in any way in the preparations of food products and beverage substances in the coloration of paper for wrapping alimentary substances and in the coloration of vessels which are employed to preserve the same, are:

(A) INORGANIC COLORS.

No	Color.	More common name.	Harmful substance contained.	More noted synonyms or diversity of the same color.
1.	Azure	Indigo of Copper.	- Copper	Mineral blue, English blue, Hamburg blue, lime blue, copper blue, Cassels blue, Neuwied blue, Azurite, Armenian Stone, Azure Crisocolla.
2. 3.	Azure Azure	Mountain Blue Azure Ashes (Azurite)	Copper Copper	
4.	Yellow	Chrome Yellow	Lead and Chrome	Chrome Yellow, Chrome Orange, Chrome Red, Cologne Yellow.
5.	Yellow	Cassels Yellow	Lead	Mineral Yellow, Montpelier Yellow, low, Paris Yellow, Verona Yellow, Turner Yellow, Chemical Yellow.
6.	Yellow	Naples Yellow	Antimony and Lead	
7.	Yellow	Orpiment	Arsenic	
	Yellow	Realgar	Arsenic	Risigall.
9.		phate	Cadmium	Brilliant Yellow.
10.	Yellow	Musive Aurum	Tin	
			Lead	
12.		Marsicot or Lith- argyrum	_ •	
13.	Yellow	Yellow of Bar- ium	Barium	Ultram. Yellow, Chromate of Bar- ium.
14.	Yellow	Yellow Bottom of Gold	Zinc	
15.	Green	Green Cinnabar		Oil Green, Chrome Green, Naples Green.

(A) INORGANIC COLORS.—Continued.

No.	Color.	More common name.	Harmful Substance Contained.	More noted synonyms or diversity of the same color.
16.	Green	Green Millory	Lead	
17.	Green	Bremen Green	Copper	
18.	Green	Verdigris	Copper	
19.	Green	Mountain Green	Copper	Malachite Green, Brunswick Green, Artificial Mala- chite.
	Green	Scheele Green	Copper and Arsenic	Patented Green, Imperial Green, Cassels Green, Paris Green, Leipsig Green.
20.	Green	Schweinfurt Green	Copper and Arsenic	Kirchberg Green.
20.	Green	Vienna Green	Copper and Arsenic	
20.	Green	Paolo Veronese	Copper and Arsenic	
20.	Green	English Green	Copper and Arsenic	
21.	Green	Mineral Green	Arsenic, Lead, Copper, Mercury	
22.	Red	Cinnabar	Mercury	
2 3.	Red	Red of Antimony		Antimoniate of Cinnabar.
24.	Red	Minium	Lead	
25.	Red	Chromate of Red Lead	Lead	Saturn Red.
26.	Red	Lithargyrum	Lead	
27.	White	White of Lead	Lead	White of Lead, Cerusa,
				Krems White, Kremitz White, Vienna White, London White, Holland White.
28.	XX71:4-	Gulphoto of Took	L cod	TIOHALU WILLE.
	White	Sulphate of Lead	Zinc	
2 9.	White	White of Zinc		
30.	White	White of Grif	Zinc	

Sulphate of copper is permitted to be used in conserves of green vegetables at the proportion of a tenth of a gram. of metallic copper for each kilo of conserved material.

(B.) ORGANIC COLORS.

Forbidden to be used are:

Gamboge—Artificial coloring matters from coal tar, except the following:

Chrysoidin, Azoflavin, Rocellin, Ponceau, Bordeaux, Biebrich Scarlet, Naphthol Yellow S, Fuchsine, Gentian.

Not allowed are the colors, either organic or inorganic, not stated in the present list, which contain harmful substances (mixtures of Antimony, Arsenic, Barium, Cadmium, Chrome, Mercury, Lead, Copper, Tin, Zinc) or other harmful substances.

The present prohibition is not applicable in cases of coloration of vessels with incorporated harmful colors, when this coloration is made in such a way that it cannot be imparted to the beverages or to the food products they may come in contact with.

We order, etc., Rome, February 7th, 1892,—Humbert. Nicotera.

Royal Decree, January 29th, 1893, No. 132, regarding the adding of artificial coloring matters to the list of the harmful colors:

Humbert I., by the Grace of God and the Will of the Nation, King of Italy, having examined the law regarding the public health and having examined the Royal Decree February 7th, 1892, No. 55, which approves the list of the harmful colors, and having heard the opinion of the meeting of the Board of Health, and having heard the meeting of the Ministers, on the proposal of our Minister and Secretary of State for the Interior affairs, we have decreed and decree:

ART. 1. Tropæolin is to be added to all the artificial coloring matters from coal tar which are not included in the list of harmful colors, approved with Royal Decree February 7th, 1892, No. 55, Part 1st, Table B., Organic Colors. The said table is then modified thus:

(B.) ORGANIC COLORS.

Forbidden are:

Gamboge—Artificial coloring matters from coal tar, except the following:

Chrysoidin, Tropæolin, Azoflavin, Rocellin, Ponceau, Bordeaux, Biebrich Scarlet, Fuchsine, Naphthol Yellow S, Gentian.

We order, etc., Rome, January 29th, 1893.—Humbert. G. Giolitti.

Royal Decree March 24th, 1895, No. 101, modifying the Part B. (Organic Colors) of the list of the harmful colors.

Humbert I., by the Grace of God and the Will of the Nation, King of Italy, having examined the law regarding the tutelage hygiene and public health; having examined the Royal Decree February 7th, 1892, No. 55, which approves the list of the harmful colors; having heard the opinion of the meeting of the Board of Health; on the proposal of our Minister Secretary of State for the Interior affairs, President of the meeting of the Ministers, we have decreed and decree:

ART. 1 The Part B. (Organic Colors) of the list of the harmful colors is modified as follows:

Forbidden are:

Gamboge.

Picric Acid.

Dinitrokresol—Mixture of the Alkaline salts of Dinitro-O-Kresol and Dinitro-p-Kresol (Substitute for Saffron—Victoria yellow, Victoria Orange, Aniline orange), Martius yellow—Dinitro-B-Naphthol (Naphthol yellow, Naphthalin yellow, Manchester yellow, Saffron yellow, Golden Yellow, Methanilic yellow, Azo-Diphenilamin (Orange Color M. N. Tropæolin F.).

The last but one line of the No. 1 is modified as follows.

Not allowed are the colors, either organic or inorganic, not mentioned in the present list, which contain the same harmful substances (mixtures of antimony, arsenic, barium, cadmium, chrome, mercury, lead, copper, tin, zinc, under any form whatsoever) and all other harmful substances.

We order, etc., Rome, March 24th, 1895.—Humbert. Signed F. Crispi.

FRANCE.

ARTIFICIAL COLORING AND FOOD STUFF HYGIENE.

Ordinance of the Police Commissioner of June 15th, 1862, concerning coloring of sweetmeats, food products, etc., and the utensils and the vessels of copper and other metals.

Considering that grave accidents have occurred either by the use of poisonous materials for coloring purposes of sweetmeats, sugar plums, food products and liquors, either from the bad quality or adulteration of food stuffs or by the bad condition or the nature of the vessels in which the dealers in food stuffs, the restaurant keepers, the fruit dealers, the grocers, etc., prepare or conserve the food products which they offer for sale, and considering that accidents have been equally caused by papers colored with toxic colors in which sweetmeats and eatables are wrapped and were so offered to the public. (Law of August 16-24, 1790, and of July 22d, 1791; the decree of the 3rd brumaire year IX.; the law of March 27th, 1851, and the articles 319, 320, 471, § 15, and 477 of the Penal Code;..... the police ordinances of July 20th, 1832, November 7th, 1838, September 22nd, 1841, and February 28th, 1853;the ministerial instructions dating October 25th, 1851, concerning the waters of orange flowers, those of October 20th, 1851, and April 7th, 1852, concerning the manufacture of syrups, and the one of April 20th, 1861, relative to the tinning of utensils for the use of food products;the reports of the Board of Public Hygiene and of Salubrity of the Department of the Seine, ordain as follows:

TITLE I.

ART. 1. It is expressly forbidden to use any mineral stuff, excepting Prussian Blue, Ultramarine, chalk (carbonate of calcium) and ochres to color sweetmeats,

sugar plums, pastilles, liquors and any sort of sweetmeats or other food products.

It is equally forbidden to use for the coloring of sweetmeats, liquors, etc., vegetable stuffs injurious to health, especially the gamboge and aconite. The employment of these materials is equally prohibited for the purpose of clarification of syrups and liquors.

ART. 2. It is prohibited to wrap or to enclose sweetmeats in white papers smoothed or colored by mineral stuffs, except Prussian Blue, Ultramarine, ochres, and chalk.

It is prohibited to place sweetmeats or conserved fruits in boxes papered inside or outside with papers colored with materials prohibited by the present ordinance and to cover them by cuts of these papers.

The same law applies to flowers or other artificial objects serving for the decoration of sweetmeats, etc.

ART. 3. It is prohibited to include any fulminating preparation in the composition of sweetmeat envelopes.

It is equally forbidden to use metallic wires for the support of flowers, fruits and other sugar and pastry confections.

ART. 4. The wrapped envelopes must bear the name and address of the manufacturer or merchant; the same applies to the bags in which the bonbons or sweetmeats will be offered to the public.

The bottles containing colored liquors must bear the same indications.

ART. 5. It is prohibited to introduce in the interior of bonbons and pastries metals or metallic com-

positions of a nature forming compositions injurious to health.

The metal leaves applied to sweetmeats must be of gold or fine silver only.

The metal leaves introduced in the liquors must also be of gold or fine silver.

- ART. 6. The syrups containing glucose (Fecula syrup, starch syrup) must bear the common denominations of "syrup de glucose" to avoid misunderstanding. Apart from this indication these bottles must bear the following label: "liqueur de fantaisie a l'orgeat, a la groseille," etc., etc.
- ART. 7. Annually or oftener, if there is cause, visits must be made to the manufacturers and retailers in order to make sure that the conditions prescribed by the present ordinance are observed.
- ORDINANCE of the Police Commissioner of May 21, 1885, concerning the manufacture, the sale and the offering for sale of colored liquors, sweetmeats, bonbons, sugar-plums and pastilles, the use of colored papers to wrap food stuffs and the offering for sale of food stuffs so wrapped.
- See:..... the law of August 16th-24th, 1790, and the one of July 22nd, 1791;..... the decrees of the Consuls of 12th messidor year VIII. and 3rd brumaire year IX. and the law of August 7th, 1850;..... the articles 319, 320, 471, §§ 15 and 477 of the Penal Code; the law of March 27th, 1851;..... the Police ordinance of June 15th, 1862;..... the Police ordinance of June 8th, 1881;.... the Police ordinance of July 3rd, 1883;..... the law of April 5th, 1884;.....

the ministerial instructions of March 30th, 1885; we ordain:

ART. 1. Confectioners, distillers, grocers and all merchants in general are expressly forbidden to employ for the coloring of sweetmeats, pastilles, sugarplums, liquors and food products any of the below named materials:

Mineral Colors:

Copper compositions: Azurite, mountain blue.

Lead compositions: Protoxide of lead, red lead, mine orange, lead oxychlorure, Cassels yellow, Turner yellow, Paris yellow, lead carbonate, white of lead, ceruse, white of silver, lead antimoniate, lead chromate, Naples yellow, sulphate of lead, Chrome yellow, Cologne yellow.

Chromate of barium.

Arsenic compositions: Arsenate of copper, Scheele green, Schweinfurt green.

Sulphate of Mercury: Vermilion.

Organic Colors:

Gamboge: Aconite.

Colored stuffs deriving from aniline and its homologues, as the Fuchsine, Lyon blue, flavaniline, methylene blue.

Phtaleines and their substituted derivatives.

Eosin, erythrosin.

Colored materials containing among their elements the nitric vapor like the naphthol yellow, Victoria yellow.

Colored materials prepared by the aid of diazoic compositions like tropæolines, xylidine red.

ART. 2. The manufacturers and all merchants in general are forbidden to sell or to offer for sale sweet-meats, pastilles, sugar-plums, liquors and food stuffs colored by above mentioned colors.

It is equally forbidden to employ for the wrapping of food stuffs papers colored with these colors and to offer for sale food stuffs thus wrapped.

ART. 3. Attention is called to the ordinances of the Police of June 8th, 1881, and July 3rd, 1883.

The Police ordinance of June 18th, 1862, is maintained in those of its dispositions which are not contrary to the present ordinance.

ART. 4. The contraventions will be prosecuted according to the law before the competent courts.

ORDINANCE of the Police Commissioner of December 31st, 1890, concerning the coloration of food stuffs, the papers and envelopes used to wrap them and the vessels which will contain them.

See:....the laws of August 16-24, 1790, and July 22nd, 1791;.....the Consuls' decrees of 12th messidor year VIII. and 3rd brumaire year IX. and the law of August 7th, 1850;.....the Police ordinances of May 21st, 1885, and February 5th, 1889;.....the ministerial circulars of December 17th, 1888, and January 16th, 1889, relative to the employ of pewter leaves to wrap the food stuffs;.....the advice emitted by the Consulting Committee of Public Hygiene of France and the instructions of the Secretary of State of May 7th, 1889, August 29th and September 29th, 1890; we ordain which follows:

ART. 1. The use of the colors below mentioned is

prohibited for the coloration of any food products of whatever description:

Mineral Colors:

Copper compositions: Azurite, mountain blue.

Lead compositions: Protoxide of lead, red lead, mine orange, carbonate of lead, white of lead, ceruse, silver white;....lead oxychlorure (Cassels yellow, Turner yellow, Paris yellow);....lead antimoniate (Naples yellow);....sulphate of lead;....Chromate of lead (Chrome yellow, Cologne yellow).

Chromate of Barium.

Arsenic compositions: Arsenate of copper, Scheele green, Schweinfurt green.

Sulphate of Mercury: Vermilion.

Organic Colors:

Gamboge: Aconite.

Coloring stuffs obtained from coal tar like fuchsine, Lyons blue, flavaniline, methylene blue; phtaleines and their substituted derivatives, eosin, erythrosin.

Coloring stuffs prepared with the aid of diazoic compositions like tropæolines, xydiline red.

ART. 2. As an exception it is permitted to employ for the coloration of candies, pastilles, sweetmeats, ices, fruit pastries and certain liquors which are not naturally colored, like the green mint, the colors below mentioned, deriving from coal tar, by reason of their restrained use and the small quantity of coloring stuffs which these products contain:

Pink Colors:

Eosin (tetrabromo-fluorescein).

Erythrosin (methylic and ethylic derivatives of eosin).

Bengal Rose, Phloxin (iodine and bromine derivatives of fluorescein).

Bordeaux Red (obtained by the action of sulphonaphthol derivatives upon diazoxylenes).

Acid Fuchsine (without arsenic and prepared by the Coupier system).

Yellow Colors:

Acid Yellow, etc. (derivatives of sulpho naphthol). Blue Colors:

Lyons Blue, Light Blue, Coupier Blue, etc. (derivatives of triphenilic rosaniline or dry diphenylamin).

Green Colors:

Mixtures of above blue and yellow colors.

Malachite Green (chlorhydric ether of the tetrametyldiamidotriphenylcarbinol).

Violet Colors:

Paris Violet or Violet of metylaniline.

ART. 3. The use of colors below mentioned is prohibited for coloring of papers and cardboards employed to wrap food materials of any nature whatsoever.

Mineral Colors:

Copper compositions: Azurite, mountain blue.

Lead compositions: Protoxyd of lead, red lead, mine orange;...carbonate of lead (white lead, ceruse, white silver);....Lead oxychlorures

(Cassels yellow, Turner yellow, Paris yellow); Lead antimoniate (Naples yellow); Lead sulphate; Chromate of lead (Chrome yellow, Cologne yellow).

Chromate of barium.

Arsenic compositions: Arsenate of copper, Scheele green, Schweinfurt green.

Organic Colors:

Gamboge: Aconite.

ART. 7. The offering for sale of products, objects and utensils, the manufacture of which is forbidden by the present ordinance, is prohibited the same as their manufacture.

ART. 8. Attention is called to the Police ordinances of May 21st, 1885, and February 5th, 1889.

ART. 9. Violations of this ordinance shall be published and posted and will be prosecuted in accordance with the law before the competent courts.

ARTIFICIAL COLORING.—Many liquors are not accepted by the buyer unless they are colored. Certain colorations are given naturally by the infusions themselves, like those of cassie, raspberries, etc.; others by tinctures of amber, benjoin of cachou, etc., in alcohol; finally many are taken from tinctorial materials like the cochineal by decoction in boiling water, etc.

For coloring red is used cochineal prepared with alum and creme of tartar, cudbear (pulverized orchil), orchil paste, myrtle berries, hematine, coloring principle of campeche, sandal wood, red of lacque, wood of Fernambouc. The blue is obtained from indigo treated by sulphuric acid. The violet blue is obtained by the cochineal to which is added calcinated alum and a little liquid ammonia. The violet is also produced by the mixture of blue and red. The yellow is obtained from saffron, curcuma, ginger. The green is prepared by the yellow, saffron for example, and indigo blue. The green color of plants, chlorophyll, is also extracted by boiling in alcohol leaves of balm mint, nettles, spinach, mint, wormwood, cassie, mountain wormwood.

Finally yellow color is often obtained by the use of caramel, especially much used by the liquor dealers. The caramel is obtained by burning of sugar.

The prejudice against the so-called aniline colors is easily explained. About the middle of the last century, when the first colors of this class appeared on the market, their toxic quality was quickly determined by proper experiments. These colors, especially Mauveine, Fuchsine, Aniline Blue, Aniline Red, etc., were at that time made from aniline and very frequently retained, as impurities, some parts of the arsenic and quicksilver which were employed in their manufacture.

As was later proven, beyond a doubt, by proper physiological experiments, the poisonous quality of the colors was not due to the colors proper but to the above mentioned arsenic and quicksilver impurities. Sonnenkalb, Bergeron, Clouet and others proved by experiments on human beings as well as on animals that even large doses of these colors could be partaken of without any detrimental effect whatsoever, "if same were free of the poisonous impurities." But science

did not stop at that, and to-day these colors are no longer produced with the aid of arsenic and quicksilver but by the Nitrobenzol process.

Grandhomme used a so-produced fuchsine in his tests upon rabbits and chickens with the following results:*

Two rabbits received for several weeks with their food daily each 0.5 gr. fuchsine. The animals remained perfectly healthy and in good condition; the urine showed no albumen. Then the rabbits received for two weeks over 1 gr. daily without the slightest ill effects. The same result was obtained by continually feeding a chicken with oats which had been colored with fuchsine. Grandhomme also reports that at the Hoechster Farbwerke of 52 workingmen who were continually employed in the Fuchsine room

none of these workingmen suffered of diarrhoea, colic, etc. Their urine was examined every Saturday, and after having worked all week in a room which naturally was always filled with the fine dust of Fuchsine, the urine was free of albumen. These and a great many similar tests made by absolutely reliable investigators have proven beyond a doubt that these colors are harmless. Why then forbid their use? Simply because once upon a time they contained poisonous admixtures, or simply because once upon a

^{*} Weyl, Die Theerfarben.

time there existed a well founded prejudice against these products.

This should by no means indicate that all the coal tar colors are harmless. Just the contrary, there are certain colors the use of which should absolutely be forbidden. By their thorough physiological experiments Weyl, Cazeneuve, Lepine, etc., have proven beyond a doubt the detrimental effect of certain coal tar colors and on account of their importance, I will copy their reports (translated and abbreviated).—Weyl, Die Theerfarben.

NITROSO COLORS.

 $I.\!-\!Dinitrosoresorcin.$

 $(\mathrm{C_6H_4N_2O_4})$

is produced by the action of sodium nitrite upon a solution of resorcin in diluted acetic acid under low temperature.

Very little soluble in cold water or alcohol. More readily soluble in hot water and in hot alcohol.

Insoluble in benzol or ether. It explodes if heated to 115°.

The alkaline solutions discolor quickly into a brownish shade when exposed to air.

The watery solution is colored green upon addition of ferrous salts. The green solution is discolored through reducing agents.

It produces green color in cotton which had previously been treated with iron salts. This color is fast to light and soap. The thereby produced green color is called resorcin green, Alsace green or solid green.

Application through the Stomach. Test 2—Dog of 11550 Grams.

June 18th—2 gr. with a little soda by means of tube.

"19th—Animal lively. Urine very little, dirty dark brown, neutral. Urine is colored dark green upon addition of iron salts. This green color is retained in diluted acetic or hydrochloric acid.

2 gr. through tube. Urine 600 Ccm dark brown.

Traces of albumen. Iron reaction very pronounced.

A little alkaline. Does not reduce Fehling's solution.

June 20th—2 gr. through tube. Dog lively. Brown hard fæces.

June 21st—3 gr. through tube. Dog lively. No albumen.

June 22nd—Dog lively. Weight 11140 gr. Loss about 400 gr.

Test 3—Dog of 5500 gr.

July 13th—1 gr. through tube.

"14th—Has eaten very little. Urine dark brown, almost black, colored green with ferrous sulphate, and forms gradually a green precipitate.

July 15th—2 gr. through tube.

" 16th—Urine colored green with ferrous oxide. No albumen. Does not reduce alkaline copper solution. Acids produce black flaky precipitate.

July 17th—Dog lively. 3 gr. through tube. Urine alkaline. Color deep black.

July 19th and 20th—Dog lively. Urine contains some albumen. Diluted sulphuric acid produces a flaky

brown precipitate. After filtration precipitate is readily dissolved in water and precipitated out of the filtered solution through diluted sulphuric acid. The body is colored green by ferrous oxide. The filtrate of the precipitate produced through the acid is not colored green again with ferrous oxide even after neutralizing.

Hypodermic Application. Test 4—Dog of 5250 gr.

July 4th—1 P. M. 1 gr. dissolved in 10 Ccm water and a little soda is injected under the skin of the back. In the evening very weak. Urine 50 Ccm, colored almost black. Addition of iron salts does not produce green color. Presence of sulphates. Traces of albumen. Upon addition of acids a brown flaky precipitate is produced which is soluble in alkalies. Upon distillation with hydrochloric acid no precipitate could be obtained in the distillate with bromine water.

July 5th—Dog indifferent. Refuses absolutely all nourishment. Dead about 2 o'clock P. M.

July 6th—Dissection. Corpse stiff and rigid. All abdominal organs hyperaemic, lungs hyperaemic, heart contains a great deal of non-coagulated blood.

None of the examined parts of the corpse show green coloration with ferrous salts.

The herewith cited tests show that the Dinitrosoresorcin is harmless to the dog even if administered in large doses through stomach, whereas upon hypodermic injection as little as 0.19 gr. per kilo of the animal is sufficient to kill the dog within 24 hours.

II. Naphthol Green B.

$$(C_{20} H_{10} N_2 O_{10} Fe Na_2 S_2)$$

Is the iron soda salt of the Nitrosonaphtholsulpho acid.

It is a dark green powder, readily soluble in water, producing green color. If dusted in concentrated sulphuric acid appears golden yellow. No precipitate is produced upon diluting of the sulphuric acid with water.

Diluted acids do not change the watery solution. Concentrated acids produce yellow color. Upon addition of alkalies the green color is restored, providing it has not been affected for too long a period by the acid.

The green solution is colored yellow when heated with a solution of caustic soda. Ether shaken with the alkaline solution remains colorless. The green solution gradually loses its color when heated with stannous chloride and hydrochloric acid.

When heated upon a sheet of platinum a residue is obtained which contains sulphate of iron.

Application Through the Stomach.

Test 1.—Female Dog of 5800 grams.

May 13th and 14th—Urine contains traces of albumen.

'15th—One gr. dissolved in a little water through tube.

May 16th—Animal very lively. Conjunctiva colored intensely green. Urine greenish. 1 gr. through tube.

- May 17th—1 gr. stomach tube. Urine green.
 - " 18th—5 gr. (!) through tube. Animal lively.
 - " 19th—Appetite undisturbed. Animal lively. Moderate diarrhœa.

Test 2—Dog of 4800 gr.

May 12th to 14th—Urine free of albumen.

"15th—2 gr. through tube. Urine dirty yellow green. No albumen. No iron could be found by means of the well-known reagents. The urine cooked with fuming nitric acid for \(\frac{3}{4} \) of an hour barely contained traces of iron.

May 16th—Dog normal.

- "17th—2 gr. through stomach tube. Animal unchanged. Lively. Eats good. Urine yellow green. No sugar. No albumen.
- May 18th—Very lively. Normal green colored faeces. Watery extract of the faeces when treated with ammonia or a solution of caustic soda discolors green. When treated with acids discolors red. Urine yellowish green. Urine acts the same as the watery extract of the fæces. No albumen. No sugar. The urine is gradually colored black, commencing at the top. By a mistake the animal receives 2 gr. of safranin. Mild diarrhæa.

Hypodermic Application.

Test 3.—Female Dog of 5650 gr.

May 20th to 23d—Urine free of albumen?

"24th—Hypodermic injection of 2 gr. in 25 water. Very lively. Has eaten. Conjunctiva, flesh surrounding teeth and gums colored green. May 25th—Hypodermic injection of 2 gr. in 25 water. Animal lively.

May 26th—2 gr. hypodermic injection.

- " 27th—No injection.
- " 28th—2 gr. hypodermic injection.
- " 29th—No injection. Animal lively. No abscesses (see tests 4 and 5). Diarrhœa.

Test 4.—Dog of 5015 gr.

May 22d and 24th—Traces of albumen.

" 25th—Hypodermic injection of 2 gr. in 25 water. 20 minutes after injection, conjunctiva, flesh around teeth and gums are colored green. Animal lively. Little urine of an intensely green color.

May 26th—2 gr. hypodermic injection. Animal lively.

- " 27th—No injection.
- " 28th—2 gr. hypodermic injection. Urine colored intensely green. Is colored intensely red with acids.
- May 29th—Animal very lean. No injection. Urine when made slightly acidulous with sulphuric acid dyes wool intensely dark green.

May 30th—Animal weak, feverish. Inner surface of ears green, as well as also the conjunctiva.

June 1st—Many abscesses upon the back.

" 2d—Death. Six abscesses with pus upon the back. Dissection, exactly the same as in the following test.

Test 5.—Dog of 5600 gr.

May 18th—Hypodermic injection 2 gr. in 25 water. 20 minutes after injection the conjunctiva are colored green. May 19th—Hypodermic injection 2 gr. Urine green.

- " 20th—Hypodermic injection 2 gr.
- " 21st—2 gr. Green urine dyes wool intensely green.
- " 22d—Dog lively. No abscesses. Weight 5450 gr., or a loss of about 150 gr.

May 24th—Several abscesses upon the back.

" 26th—Animal very weak. Was killed. Dissection: Under the skin of the back three big abscesses, one of which, when pressed, discharged a greenish pus without bad odor. Peritoneum, pericard, endocard, and pleura colored intensely green. Liver and spleen also colored green. The glomoeruli in the kidneys are not colored, whereas the urine channels are colored green.

The tests 1 and 2 in which from one to five gr. daily of Naphthol Green have been applied directly to the stomach have proven the non-toxic quality of this color when partaken through the stomach, whereas hpyodermic applications in two or three cases produced abscesses and septic fever. An infection through the syringe is not probable, as other animals upon whom the same instrument had been used remained absolutely free of abscesses. Also the cage could not be blamed. I rather must consider the color poisonous if applied hypodermically.

The dog 3, I must surmise, was not treated sufficiently long and therefore appeared healthy when the test was finished. Very interesting is the pronounced green coloration of the conjunctiva and of the inner surface of the ear, appearing about ½ hour after injection.

NITRO COLORS.

I. PICRIC ACID.

$$C_6 H_3 N_3 O_7 = C_6 H_2 (OH) (NO_2)_3 = NO_2$$
 $OH NO_7$ NO_2

is Trinitrophenol.

Is mostly produced through the effect of nitric acid upon phenolsulpho acid. When dusted in sulphuric acid, colorless.

The aqueous solution is not clouded upon addition of a few drops of diluted hydrochloric acid.

Ether withdraws picric acid out of an acidulous solution. The ether becomes yellow colored. When cyanide of potassium is added the ether extract is colored reddish brown. The test with cyanide of potassium may also be made with a watery solution.

A solution of copper oxide in ammonia produces a yellow crystalline precipitate even when greatly reduced. The precipitate is dissolved to a clear liquid in hydrochloric acid. The solution in hot water is colored dark brownish red upon boiling with cyanide of potassium.

Copper picrate is soluble in alcohol.

Ammonium picrate does not produce a precipitate with a solution of caustic soda.

Through a reduction with alcoholic sulphate of ammonium, Dinitroamidophenol is formed which is soluble with red color.

The hydrochloric solution of stannous chloride reduced to Triamidophenol, which is transformed into blue colored Diamidoamidophenol, upon addition of a

little ferric chloride. Ferric chloride produces with picric acid a reddish yellow precipitate, readily soluble in water.

To observe picric acid in fiber or in food products, it must be isolated, and for this purpose it is best to obtain some in an ether solution; the latter is then shaken with some alkaline. With the alkaline of the picric acid the above mentioned tests can be made.

Picric acid was formerly used a great deal alone and mixed with other colors to dye silk, wool (not cotton) and artificial flowers, yellow.

It is supposed to have been used also as color for food and liquid products (beer). Even as a medicine (see below) it was prominent at one time.

In Germany its use as a color for food products, etc., has been prohibited by law on account of its poisonous qualities, since May 1st, 1888. The poisonous qualities of picric acid have been, however, frequently over-estimated.

Erb gave a rabbit of a weight of 1700 gr. during 90 days daily one grain (like 0.06 gr.) potassium picric. Occasionally it produced diarrhœa and loss of weight. Worse symptoms could not be observed. A rabbit of 2065 gr. died only after it had taken within 19 days 42 grains (equal to 2.52 gr.) of the picric acid.

A very young dog received from

April 21st to 26th, daily 4 gr. sodium picrate.

From April 28th to May 9th—daily 6 grains sodium picrate, that is, in the course of about three weeks 96 grains (equal to 5.76 gr.) sodium picrate, without producing any dangerous symptoms. Then the same animal received on

- May 13th—20 grains (like 1.2 gr.) sodium picrate at once. Within the following days the dog grew very weak. Considerable diarrhœa and Dyspnœa made their appearance.
- May 14th—Again 10 grains (0.6 gr.) were administered which, however, produced nausea. Evening again 6 grains (0.36 gr.).
- May 15th—The animal is lively and again receives 4 grains (0.24 gr.) and on the same evening again 12 grains (0.72 gr.).
- May 16th—Very weak. Hypodermic injection of 3 grains (0.16 gr.) Sodium Picrate. Heavy vomiting follows.
- May 17th—Hypodermic injection of 12 grains (0.72 gr.).
- May 18th and 19th—Animal improves remarkably. Besides a considerable yellow coloring of the conjunctiva and of the outer skin it shows no abnormities.
- May 20th the poor animal dies after receiving 22 grains (1.32 gr.) Potassium picrate.

The dog had received the enormous dose of 175 grains (10.5 gr.) in a period of 4 weeks, of which 15 grains (0.9 gr.) Sodium resp. Potassium picrate had been administered hypodermically. After having partaken of 143 grains (8.5 gr.) the dog was still fairly well.

Dogs are, therefore, in spite of the prostration of strength produced by picric acid and in spite of the considerable destruction of the blood, very much able to resist this material.

We are also very well informed of the effect of

picric acid and its salts upon the human body by means of therapeutic applications and through cases of poisoning. Daily doses of from 9 to 15 grains Potassium picrate (0.54 to 0.9 gr.) can be easily endured for quite some time by healthy and grown-up people. Generally after 24 hours appears a distinct yellow coloring of the skin and the conjunctiva. The urine becomes dark colored and contains besides other ingredients, also small quantities of picric acid.

Picric acid does not agree with children and weakly, feverish, grown-up people.

Picric acid used to be considered formerly as a substitute for quinine in intermittent fever. Doses of 5 to 15 grains (0.3 to 0.9 gr.) potassium picrate per day were given apparently without results.

It was also prescribed for the driving off of worms of the intestines. It is useless against Trichinosis and Cysticercus. For tape-worms, etc., however, the effect of the picrates has been praised. Picrate acid has furthermore been used successfully against whooping-cough, dyspepsia, chlorosis, itch, chancre, etc.

Only very few cases of poisoning of human beings by picric acid have been reported. None of these was fatal.

In the case of Adler, a 16-year old girl took a teaspoonful of picrate acid or about 3 to 5 gr. She vomited immediately and also had diarrhea. The sclerotic and the skin of the entire body showed an intensive dark yellow, almost brown coloring, which made the patient look icteric. The visible mucous membranes were pale. The fingers of both extremities were bent in the Metacarpo-Phalangeal joints, in

the Phalangeal joints, however, stretched like in cramps, they could not be moved actively by the patient. The blood contained a great many white and few red blood particles. Ludwig could prove picric acid in the urine. After eight days, the girl had fully recovered.

The aforesaid notices show conclusively, that while picric acid has to be counted among the poisonous materials, its toxic quality is considerably smaller than generally considered. However, to prohibit its use as coloring matter for food products and liquids, which has been done by imperial law, is fully justified.

II. SAFFRONSURROGATE (DINITROKRESOL).

As Saffronsurrogate, golden yellow, Victoria yellow, Victoria orange, aniline orange, a coloring matter has been named which principally represents Potassium or ammonium salts of Dinitrokresol. It is obtained by treating Kresolsulpho acids with nitric acid.

Potassium and ammonium salts are readily soluble in alcohol or water.

The concentrated solutions are orange colored; the weaker are yellow colored.

The salts of Saffronsurrogate explode upon heating. The commercial goods are mixed with about 40% hydrochlorate of ammonia so as to make them non-explosive and transportable.

1. Dusted in concentrated sulphuric acid remains colorless. The sulphuric acid solution does not produce a precipitate if diluted with water.

- 2. The aqueous solutions of Potassium or ammonium salts upon addition of muriatic acid become almost colorless or become a trifle yellowish colored. At the same time the free Dinitrokresol is precipitated in little yellow-colored needle shaped crystals. The precipitate is soluble in alcohol. The free color acid in the acidulous solution is absorbed by ether and becomes thereby faintly yellow colored. Alkali added to the ether extract is colored yellowish brown.
- 3. The aqueous or alcoholic solution of the coloring matter becomes colored dark brown by heating with cyanide of potassium.
- 4. The aqueous solutions of commercial Saffronsurrogate are not precipitated even after long standing by ammoniacal copper solution. Sometimes after 24 hours a little flaky precipitate is produced.
- 5. The dry salts of the Dinitrokresol explode when heated.
- 6. Ferric Chloride produces in the watery solution a slightly yellowish precipitate which is easily soluble in water. The solution heated with ferric chloride becomes reddish colored. In cooling a flaky precipitate is produced.
 - 7. Liquor sodæ does not produce any precipitate.
 - 8. Acid solution of stannous chloride produces:
 - a. By addition of ammonia, red coloring.
 - b. By addition of ferric chloride, orange yellow solution.

Its use.—Almost exclusively for yellow coloring of food and liquid products, such as noodles, liquors and pastries. Orange color of silk and wool produced by Dinitrokresol fades easily and is therefore used but very rarely.

Saffronsurrogate, as shown in the following examples, is a strong poison.

A. TESTS ON RABBITS.

1. Stomachical Application.

Animals to whom 0.25 gr. Dinitrokresol salt dissolved in a little water were administered by means of the stomach tube showed the following symptoms:

Shortly after poisoning, the animals were usually as lively as before. They jumped about in the room and did not show the least abnormity. Soon, however, the respiration became more frequent. The animal remained perfectly quiet in its place, and tumbled occasionally over on its side. In trying to walk ahead the hind legs were drawn The mouth touched the floor; it was then raised The animal was still able to move ahead. The pupils were mostly dilated. In some cases, however, they become contracted shortly before Respiration after awhile became extraordinarily frequent, it stopped occasionally, then the animal was lying continually on its side, the head touched the floor, the eyes were opened wide, the conjunctiva bulbi (the white of the eyes) insensitive, the pupils greatly dilated, the extremities began to twitch, muscular cramps appeared. Cheyne-Stokes respiration phenomena were mostly observed.

The intervals between respirations became greater after a while, up to 10 to 15 seconds. Death set in through choking, frequently after the head was thrown backward and after ordinary short-lived cramps had preceded. In two cases (I and III) of the following table the entire proceeding occurred within between 20 to 30 minutes. The preparation used in these tests was, as already mentioned above, almost pure Dinitrokresolkalium. In test IX death only followed after two hours. The following reports of these tests will specify what has been said.

Test IV. Rabbit of 680 gr. receives 0.17 gr. of the preparation.

12:22—Poisoning.

12:30—Animal jumps about lively.

12:54—Remains quiet.

1:16—Breathes through nostrils.

1:52—Head touches the floor.

2:00—Long intermissions between respirations.

2:10—Cheyne-Stokes. Intervals between breathing from 10 to 12 seconds.

2:45—Death.

Test IX.—Animal of 1797 gr. receives 0.45 gr. of the preparation.

12:00—Poisoning.

12:03—Heavy Dyspnœa.

12:10—Animal lies on its side.

12:12—Stretch cramps.

12:20—Head thrown backwards.

12:25—Dead.

TABLE I.

Test on Rabbit Application Through the Stomach.

ling No.	Weight of the animals in gr.	Substances received gr.		Dead After.	Remarks.	Name of the
Running		Abso- lute.	Per Kilo.		Rer	Preparation.
I. II. IV.	890 670 640 670	0.24 0.08 0.16 0.17	0.27 0.12 0.25 0.25	10 minutes. Remains alive. 15 minutes. 21 "		Polyt.
V. VI. VII.	1360 1880 750	$0.34 \\ 0.47 \\ 0.187 \\ 0.187$	$0.25 \\ 0.25 \\ 0.25$	46 " 25 "		Schuster.
VIII. IX.	680 1797	$0.17* \ 0.45$	$0,25 \\ 0.25$	20 "		Sauppe.
X. XI.	1610 1970	0.4	$0.24 \\ 0.25$	2 hours. 2 hrs. 45 min.		Bremerhav.
XII. XIII. XIV.	1870 1750 1690	$0.45 \\ 0.42 \\ 0.42$	$egin{array}{c} 0.24 \\ 0.24 \\ 0.25 \end{array}$	2 " 15 " 2 " 20 " 2 " 30 "		Mittenzwey.

^{*} Some of the material was lost in the administration.

$2. \ Hypodermic\ Injection.$

I have tried hypodermic injections on a rabbit with a preparation from Bremerhaven only. The symptons were as above described, only the animal was killed quicker than by application through the stomach.

Test XV.—Rabbit of 1825 gr.

Received 0.2 gr. of the preparation from Bremerhaven. Hypodermic injection in luke-warm water (that is 0.11 gr. per kilo.).

2:04—Injection.

2:10—Heavy Dyspnœa, beating of the flanks, ac-

tive expiration, very weak, extremities slide away from under the body of the animal.

2:40—Head falls to one side, eyes wide open.

3:00—Animal lies continually on one side, very heavy breathing with long intervals. (Almost Cheyne-Stokes type). Reflection of the pupils disappears.

3:15—Animal dead.

The second animal who, however, received only 0.06 gr. per kilo injected hypodermically showed heavy Dyspnæa but survived.

In the dissection of the animals to whom the poison was applied through the stomach, the stomach immediately attracted attention by its yellow color. The contents of the stomach were made acidulous with muriatic acid and washed out with ether. The ether extract colored green through chlorophyll (spectroscopic test), by shaking it with diluted solution of caustic soda transferred to the latter a substance which dissolved in alcohol with a yellowish red color. The green ether solution showed red fluorescence.

The alkaline solution was freed from ether by heating. After making it acidulous with muriatic acid it produced a crystalline precipitate of the nature of Dinitrokresol.

Most organs, especially liver and lungs contained much blood.

B. Tests with Dogs.

a. Stomachical Application.

Animals to whom saffronsurrogate is applied to the stomach through a tube show very characteristic

symptoms. In every case single or repeated vomiting is produced. Diarrhea is also frequently observed. If the dog has thus discharged the biggest part of the poison, it acts again within ten or fifteen minutes like a normal animal, it walks about, answers a call and eats the food offered.

Generally, however, the animal retains enough Dinitrokresol so that the other symptoms of the poisoning can be observed. In this case, a peculiar trembling of the whole body follows about ten to twenty minutes after the vomiting. Convulsive, frequently unsuccessful attempts to vomit follow, but generally only produce tough yellow-colored phlegm. Breathing is produced with difficulty and accompanied by active expirations. The animal is not able to keep on its legs. Saliva appears. It lies on one side. Cramps of the extremities set in which appear like an attack in which the animal tries to paw the air. Death generally follows with the 3rd or 4th attack.

Test I.—Dog of 6230 gr.

Following are a few reports of the tests:

Receives on January 8, 1888, about 1.5 gr. Dinitrokresol of the collection of the laboratory in 50 to 60 luke-warm water by means of tube.

12:20—Injection.

12:30—Repeated vomiting.

12:40—Trembles considerably. Hardly able to remain on its legs. Repeated vomiting.

12:45—Repeated convulsive efforts to vomit. Animal lies down on its side.

12:49—Cramps. Animal lies on its side.

12:52—Diarrhœa. Salivation.

1:00—Animal sleeps.

2:00—Animal absoluty recovered and well.

Test III—Dog of 5500 gr.

Receives on January 21st, 1888, 0.30 gr. Dinitrokresol of the laboratoy collection by means of tube.

12:10—Injection.

12:15—Vomiting.

12:20—Diarrhœa.

12:25—Animal falls on its side. Cramps. Repeated vomiting. Yellow tenacious white phlegm is discharged.

12:27—Repeated severer attacks of convulsions. Animal lies on its side. Mouth wide open, tetanic.

12:35—Third attack.

12:45—Fourth attack.

12:50—Animal dead. Muscles stiff. Dissection: Very little contents in the stomach. A few crystals of Dinitrokresol. Liver, intestines, lungs hyperæmic. No Methaemoglobin in the blood.

Test V.—Newfoundland Bastard of 14.5 kilos.

Receives on January 26th, 0.7 gr. Dinitrokresol, preparation of the Polytechnic Institute, in a little milk through the stomach tube.

1:55—Injection.

2:20—Animal quiet.

2:35—Dyspnœa. Whimpers aloud.

2:40—Salivation.

2:45—Passes urine which contains Dinitrokresol salt.

2:46—Vomiting.

2:50—Very restless.

3:30—Cramps. Whimpers aloud.

3:03—Vomiting.

3:15—Considerable Dyspnæa. Lies on its side. Strong attack of convulsions. Does not respond to strong irritations.

3:25—Dog livelier.

3:31—Little Dyspnœa.

4:00—Lively and completely recovered.

See Table II for complete list of the various tests.

b. Hypodermic Injection.

Through hypodermic injections I hoped to avoid the vomiting produced by stomachical applications. The tests proved this calculation to be wrong.

Test VI.—Dog of 6230 gr.

Receives on January 24th, 1888, 0.1 gr. Dinitrokresol, preparation of the laboratory collection, in about 10 cc. water by hypodermic injection. The animal had received before 0.3 gr. directly into the stomach; however, in spite of clearly shown symptoms of poisoning it survived.

1:21—Injection.

1:30—Heavy Dyspnœa. Vomiting.

1:30—Trembling. Light attack of convulsions.

1:57—Salivation. Light attack of convulsions.

2:00—Cramps. Tetanus of the Masseter. Tenacious phlegm in front of its mouth.

2:05—Heavy Dyspnœa. Animal lies on its side.

2:10—Rrepeated attacks of convulsions and cramps. Dog does not respond any more to calls, not even to strong irritations.

2:15—Dead. Muscles stiff. Dissection: As above. No Methaemoglobin in the blood.

Test VII.—Dog of 14.5 kilos.

Receives January 26th, the following doses of the preparation of the laboratory collection by hypodermic injection.

(Three days before the animal had received a heavy dose (0.7 gr.) of the poison, stomachical application. In spite of distinct symptoms of poisoning the dog remained alive.

10:40—0.1 hypodermic injection.

Until 12:15—A little weak, then livelier.

12:20—0.1 hypodermic injection. Animal weak.

2:00—0.2 hypodermic injection.

2:30—Active expiration. Abdominal breathing.

2:45—Dyspnœa. Reponds to a call by wagging of the tail. Weak attack of convulsions. Later completely normal.

Test VIII.—Dog of 3420 gr.

Receives January 27th, 1888, 0.1 gr. of the preparation of Bremerhaven, in about 10 ccm. water by hypodermic injection.

10:30-Injection of 0.1 gr.

11:06—Vomiting.

11:27—Renewed vomiting.

12:00—Same.

12:50—Hypodermic injection, 0.2.

12:55—Vomiting of yellowish material.

1:10—Convulsive attempts to vomit. Vomiting of yellowish material.

1:11—Weak attack of cramps.

1:16—Animal lies on its side. Strong attack of cramps. Cramps. Tetanus of the Masseter. Mouth wide open.

1:18—Very strong dyspnæa. Continued cramps.

1:20—Dead. Muscles stiff. Result of dissection as usual.

Test IX.—Dog of 5690 gr.

Receives 0.1 Saffronsurrogate from Mittenzwey (0.017 per kilo.) in about 25 ccm. lukewarm water, hypodermic injection.

10:40—Injection 0.1.

10:48—Hard fæces. Licks the spot where injection has been made.

10:51—Breathes very fast.

11:35—Sits down.

11:50—Apparently normal.

12:15—0.2 injection (hypodermic).

12:25—Breathing faster.

12:26—Vomits.

12:27—"

12:30— " Trembles.

12:31—Vomits yellow tenacious phlegm.

12:32—Weak attack of convulsions. Animal lies on its side.

12:33—Tries to get up.

12:35—Heavy attack. Cramp. Cramp of the Masseter. White foam in front of its mouth.

12:36—Heavy attack of convulsions.

12:37—Still in convulsions. Pupil reacts.

12:40—By irritation no attack is produced. Very fast breathing. Animal lies on its side.

12:45—Third attack of convulsions and cramps. 12:49—Fourth 66 66 "

12:52—Fifth " 66 " " "

" " " " " 12:55—Sixth

1:00—Seventh " " 66

" 1:02—Eighth " 66 " " 1:05—Ninth " " " 66

66 66 " 66

1:08—Tenth 1:15—Eleventh " " " 66 66

1:26—Respiration 108 (!)

1:32-120 (!)

1:38-66 148 (!)

1:39-180 (!)

1:45-120 (!)

- 1:50—Breathes slower. Lies on its side. Opens its eyes.
 - 1:52—Makes spontaneous movements with its tail.
 - 2:00—Breathes a great deal more quietly.
 - 2:10—Respiration 90.
 - 2:25—Moves the head spontaneously.
 - 2:30—Wags its tail a little.
- 2:45—Has recuperated. Still lies on its side. Lives on the following day and is apparently completely normal.

TABLE II.

Tests on Dogs.

Running No.	Weight of the animals in gr.	Substances received gr. Absolute. Per Kilo.		Dead After.	Remarks.	Name of the Preparation.
		a. Sto	machical	Application.		
I. III. IV. V.	6230 5500 5500 6230 14500	1.5 0.3 0.3 0.3 0.7	$egin{array}{c} 0.2 \\ 0.055 \\ 0.055 \\ 0.048 \\ 0.05 \\ \end{array}$	40 minutes.	Recuperates. Recuperates.	Polytech-
		b. H	b. Hypodermic Injection.			
VI.	6230	0.1 a) 0.1	0.016 0.007	75 minutes.	Deann) Dolmtoch
VII.	14500	b) 0.1 c) 0.2	$0.007 \\ 0.014$		erates.	Polytech-
VIII.	-342 0	0.1	0.029	170 minutes.		Bremerhaven
IX.	5690	a) 0.1 b) 0.2	0.017 0.035		Recup serates.	Mitten- zwey.

The above table requires little explanation. It could appear astonishing that animals which received 0.05 gr. Dinitrokresol salt through the stomach (Tests II-V) did not die in all cases. This, however, is easily understood if one considers that every application of a dose is a deception which produces as the one in question immediate vomiting. It depends clearly on chances which the experimenter

does not control, whether much, little, or as good as nothing of the administered saffronsurrogate become effective. The same is especially the case with Test I.

By hypodermic injection the proportions are as follows: Tests VI and VII are to be compared because they are undertaken with the same preparations. The animal which received 7 mgr. per kilo. (Tests VIIa and VIIb) remained alive. 16 mgr. per kilo. killed in Test VI. 14 mgr. per kilo. were not fatal for the big dog of 14.5 kilo. in Test VIIc. 29 mgr. per kilo. killed in Test VIII almost double the quantity of the dose which produced death in Test VI. But the Bremerhaven preparation used in Test VIII contained, as is mentioned later more explicitly, about 33% ammonium chloride, while the preparations of the collection of the laboratory used in all the other tests were almost pure Dinitrokresolkalium.

The animal of Test IX (test was made with the preparation of Mittenzwey) was near death, as the test report indicates.

The tests made on the dog showed the following characteristic symptoms of poisoning:

It is immaterial whether the poison was applied to the stomach or hypodermically, in all cases nausea and vomiting were the first signs of poisoning. Active expiration and dyspnœa accompanied. Then followed salivation and characteristic trembling of the whole body.

The animal mostly lay helpless on its side.

The first attacks of convulsions appeared, and mostly in the form of severe cramps. A second and third attack of convulsions followed.

The animals usually died during such an attack. A few minutes after death the muscles were found to be stiff and rigid (rigor mortis).

In several cases the animals recuperated entirely after one to two hours.

As dosis toxica resulted for the dog by hypodermic injection 7 to 10 mgr. per kilo. against the dosis lethalis 16 mgr. per kilo. for an almost pure Dinitro-kresolkalium, 29 mgr. per kilo. for the commercial preparation with over 30% ammonium chloride.

As appears from the following formulas, saffronsurrogate resembles carbolic acid and picric acid:

$$\begin{array}{cccc} C_6H_5OH & C_6H_4CH_3 \\ Carbolic Acid & Methylcarbolic Acid \\ Phenol & Kresol \\ OH & OH \\ & / \\ C_6H_2 = (NO_2)_3 & C_6H_2 = CH_3 \\ & \\ Picric Acid & (NO_2)_2 \\ Trinitrophenol & Saffronsurrogate \\ & Dinitrokresol \\ \end{array}$$

The poisoning symptoms of the Dinitrokresol correspond also in the main points with those of carbolic acid as are shown on the rabbit by E. Salkowski, on the dog by J. Munk.

One could almost call a poisoning by saffronsurrogate a carbolic acid poisoning. Only Dinitrokresol is considerably more poisonous than the carbolic acid, as the following summary will show:

	Application.	Dosis Lethalis Gr. per Kilo.		
		Rabbit.	Dog.	
Carbolic Acid.	Stomach	0.45	0.5	
Dinitrokresol Commercial Goods Dinitrokresol Pure	Hypodermic Injection	0.25	0.029 0.016	

In this table the per os applied doses are compared with those which were given hypodermically. This was done because the Saffronsurrogate if applied to the stomach causes vomiting, and it is, therefore, difficult to establish exact doses, furthermore because it seems that the dosis lethalis of carbolic acid by hypodermic injection for the dog has not been established. Taking it for granted, however, that carbolic acid affects about 50% stronger by hypodermic injection, which is surely exaggerated, then the poisonous quality of the Dinitrokresol is still considerably superior to Phenol.

A characteristic difference between Dinitrokresol and carbolic acid poisoning is shown by the producing of vomiting of the first substance.

The aforesaid communicated tests prove the Dinitrokresol to be a poison. It is, therefore, fully justified that the State should prohibit the free handling of such a dangerous stuff, and also prohibit its use for coloring or food products, liquids and also of fabrics.

A still better cause for the above is shown in the case of fatal poisoning by Saffronsurrogate (Dinitrokresol) of the human being, for the first knowledge

of which I am indebted to the courtesy of Dr. With, Police Surgeon in Bremerhaven. The circumstances are in short as follows:

On August 9, 1887, J., a married woman in Bremerhaven, whose menstruation did not set in, sent for 15 Pfg. Saffron. She swallowed the red powder 8 o'clock in the morning, was taken ill with vomiting, and died on the same day about 1 o'clock noon.

Dissection undertaken on the following day. The skins of the abdomen were pale yellow, also the conjunctiva and the mucous membrane of the mouth. No acid impressions in the mouth. In the pericardium dark yellow serum. No liquids in the pleura. In the bronchial tubes yellowish green liquid substance, also in the lungs. In the small intestine no abnormal contents. The mucous membranes of the stomach were colored with a brownish yellow pulp. The contents of the stomach showed upon diluting with water in a thin layer an intensely yellow, in a thick layer a brownish yellow red color. The urine has the same peculiar yellow coloring as the skins of the abdomen of the corpse. The urine contained no gall coloring. I cannot say anything about the uterus.

The County Court in Bremerhaven sent to me about 10 gr. of the powder of which the dead woman partook.

I have used same for toxicological and chemical tests.

a. Toxicological Tests.

They have already been described at length before. For comparison I shall again show the tests made by

me with the Bremerhaven preparation, and add to same the experiments made with the commercial product of Mittenzwey, for the reason, as will be shown later, that both products were identical.

Tests on Animals with the Preparations from Bremerhaven and Mittenzwey.

o.	Name of the Preparation.	Animal.	How Applied.	Weight of the Animals gr.	Absolute gr.		Remarks.
1 2 3 4 5 6 7 8	Bremerhaven. "" Mittenzwey Bremerhaven. Mittenzwey	Rabbit. " " " Dog	Stomach '' Hypodermic Stomach '' Hypodermic	1750 1690	0.4 0.5 0.45 0.2 0.42 0.42 0.1 a)0.1 b)0.2	0.24 0.25 0.24 0.109 0.24 0.25 0.029 0.017 0.035	" " 2 " 20 " " 2 " 30 " " 2 " 30 "

These tests show that the Bremerhaven preparation is a material which is capable of killing rabbits and dogs by stomachical application as well as by hypodermic injection, even in small doses, after a short time.

The characteristic symptoms under which the animals died have been described above.

b. Chemical Test.

The Bremerhaven preparation consisted of an orange red, soft, indistinctly crystalline powder.

When heated in a tube closed on one side it decomposes discharging at the same time nitrous fumes; when heated upon platinum it decomposes under sizzling.

In dissolving with water of ordinary temperature, one part of the powder dissolved with orange color, another part remained as a brownish black substance resembling tar; the latter when treated with warm water was completely dissolved.

The solution of the powder in water dyed silk and wool orange.

The color could be drawn off completely by hot water. The watery solution was not precipitated by liquor sodæ. Ammoniacal copper solution produced a very small flaky precipitate after 24 hours only. Upon addition of diluted sulphuric acid or muriatic acid to the watery solution a crystalline precipitate was produced. The same was repeatedly re-crystallized out of hot water; the yellow needle shaped crystals melted at 79 to 80 degrees. (The Dinitro-pkresol melts at 84 degrees, the Dinitro-o-kresol at 86 degrees.) The crystals contained nitrogen and exploded when heated quickly and were soluble in alcohol and in alkalies with orange color.

Unquestionably we had a mixture of Dinitro-Paraand Dinitro-Ortho-Kresol. There was not enough material for a further separation and for burning purposes. A quantitative definition of the substances contained in the Bremerhaven preparation was tried after the following two methods.

A. 2 gr. of the red powder were dissolved in about 300 ccm. of hot water which was mixed when still

warm with diluted sulphuric acid and set aside for 48 hours. After that time the precipitate was collected on weighed filter, washed a little with water, dried in vacuum and weighed. The yellow filtrate was shaken with ether until discolored. The ether extract was evaporated in a dish which had been weighed. The residue was weighed after drying in vacuum over sulphuric acid and considered the same as the matter collected on the filter, as Dinitrokresol.

The watery, almost colorless filtrate, freed from ether, was increased to ½ liter; same contained Potassium, Ammoniac and Chlorine. The chlorine was etermined by titrating with a silver solution and considered as ammonium chloride (NH₄ Cl), while the Potassium on account of the weighed Dinitrokresol was taken into account as Dinitrokresolpotassium.

In this way I received out of 2 gr. substance:

= 51. 8% Dinitrokresol.

Furthermore :—0.4524 Cl = 0.67 NH $_4$ Cl = 33.5% NH $_4$ Cl.

B. In the second experiment 2 gr. of powder were dissolved in about 300 gr. water to which was added an excess of diluted sulphuric acid, then immediately shaken with ether until discolored. The residue of the ether extract was dried in vacuum over sulphuric acid and then weighed.

Obtained:

Dinitrokresol..........0.984 gr. = 49.2%.

The preparation in average therefore contained in two tests $\frac{51.8 + 49.2}{2} = 50,5\%$ Dinitrokresol, which is equal to 60% Dinitrokresolkalium.

Add 33.5% of Ammoniumchloride. The rest has to be taken in account as moisture and as loss.

60 % Dinitrokresolkalium.

33.5% ammonium chloride.

6.5% moisture and loss.

100.0%

When I compared the Bremerhaven powder with the commercial Saffronsurrogates which were contained in my collection, it was found that the Saffronsurrogate of Mittenzwey in Poelbitz first in its color and then also in its chemical composition was identical with the Bremerhaven powders.

This chemical identity is further proven by a complete identity of the toxicological effects of both preparations. This point has already been described more explicitly above.

The court proceedings have furthermore proven that said Bremerhaven preparation was obtained from Mittenzwey.

It can be proven with safety on account of the toxicological and chemical tests which I stated, that said woman in Bremerhaven died through poisoning with Saffronsurrogate.

With the intention to produce abortion through a saffron powder she took in place of the genuine saffron (Crocus) the Saffronsurrogate given to her. deathly powder cost 15 Pfg. As a kilo. of Saffronsurrogate is sold by the manufacturer for about 23 marks and as the retail dealer makes at least a profit of 50%, the woman must have received for 15 Pfg. about 4.5 gr. of the poison. Had the woman weighed 75 kilo. then the fatal dose of the Saffronsurrogate of Mittenzwey would have to be considered as 0.06 gr. per kilo. human being. It has also to be emphasized that the Bremerhaven preparation could not have contained considerable quantities of other nitro combinations, especially of picric acid. I have convinced myself that the usual and commercial nitro coloring materials are precipitated by considerable dilution with ammoniacal copper solution with the exception of Dinitrokresol. Brilliant Yellow which also forms a comparatively easily soluble copper salt can not have been an adulterant of the preparation as this is precipitated through solution of caustic soda and ought to have yielded a characteristic re-action with ferric chloride.

The Bremerhaven case proves that Dinitrokresol even in small doses is a fatal poison for the human being. The free handling of such a substance ought to be prohibited by law.

3. MARTIUS YELLOW.

 C_{10} H_5 N_2 O_5 Na.

Martius yellow is named after its discoverer, Dr. C. A. Martius, in Berlin. It is also designated as naph-

thol yellow, naphthaline yellow, Manchester yellow, Saffron yellow, Jaune d'or.

- 1. Dusted in concentrated sulphuric acid, reddish yellow. The solution of color in sulphuric acid becomes milky and cloudy when diluted with water. If ether is added to the sulphuric acid solution diluted with water, the ether becomes only a little yellowish colored. If the ether is poured off very carefully, it becomes deep yellow colored upon addition of liquor sodæ. Even the alkaline solution becomes yellow to brownish yellow colored.
- 2. With cyanide of potassium the watery color solution, after considerable boiling, shows first a brown color; then the entire liquid colors itself intensely dark brown. The reaction with cyanide of potassium is the same, as it seems, in all nitro colors.
 - 3. Upon heating it explodes.
- 4. The watery solution becomes cloudy upon addition of a little acid.
- 5. The watery solution is precipitated in flakes after a little while through liquor sodæ. The precipitate is reddish.

Picric acid, Dinitrokresol, Naphthol Yellow S and Aurantia are not precipitated by a solution of caustic soda.

6. Ammoniacal copper solution produces a crystalline precipitate, even when greatly diluted. The copper salt is soluble in hot water and produces with concentrated sulphuric acid a precipitate of free Dinitronaphthol with which the ether test described under No. 1 can be made.

- 7. Through reduction with a muriatic acid solution of stannous chloride is produced:
 - a. By addition of ammonia, an orange-red solution.
- b. By addition of ferric chloride, an almost fuchsine red liquid.
- 8. Ferric chloride produces a yellowish precipitate which is colored red like the solution upon boiling.

Its uses: As Martius yellow discolors considerably and evaporates partly upon heating, it is used but very little for dyeing of wool and silk.

After G. Schulz it is used for wool and carpet printing.

It is used for coloring of food products (macaroni) in France and Italy.

There are some good tests of Cazeneuve & Lepine regarding the effects of Martius yellow upon animal organisms.

Cazeneuve and Lepine experimented with the sodium salt of Martius yellow.

To a dog of 7 kilos were given daily 0.05 gr. (per kilo?) of the pulverized color through the throat. Beginning with the second day, diarrhea and vomiting of yellow colored material. The animal refused to take any nourishment except milk. Since the 4th test day dyspnea and 41 degrees in recto. These symptoms increase. On the 6th day, gasping respiration. Rectum temperature 42 degrees C. Desire to eat has disappeared. The urine contains the applied coloring matter and albumen. The animal dies on the sixth day.

Dissection—Several intestines yellow colored.

Second test animal; dog of 22 kilos; received 0.4

gr. (per kilo?) suspended in syrup. The following day 0.5 gr. Poisoning symptoms same as dog No. 1. It is killed.

Dissection—No coloring of the intestines. Extended Hyperæmia of same.

Further experiments were made in such manner that the experimenters injected into the vena femoralis of dogs of 10 to 25 kilos 0.03 to 0.06 gr. of the coloring matter dissolved in a 0.7 per cent. salt solution (per kilo animal). The temperature of the dogs rose to 44 degrees. Heavy dyspnæa set it. Death occurred \(^3\) to 1\(^1\) hours after injection. After dose of 0.1 per kilo injected in the blood, poisoning symptoms as already described appeared also. The animals recuperated however.

I then gave to two rabbits of 1797 gr. and of 2100 gr. each 0.55 gr. of the ammonium salt and one gr. of the potassium salt of Martius yellow. No poisoning symptoms appeared in these animals.

The following experiments were made with dogs. The more readily soluble sodium salt of Martius yellow was used. It forms yellow-red needles and was made from calcium salt.

Experiment I.

Dog of 6850 gr.

March 10, 1888—1 o'clock—0.5 gr. Martius yellow (Na. salt) in about 25 water applied through stomach tube.

1:10—Considerable nausea.

About 6 o'clock—Vomiting.

March 11—10 o'clock A. M.—Animal very weak. Temperature in recto 40.8 degrees. Vomiting. Diarrhæa. In the urine traces of albumen. The urine a little darker colored than the salts applied. The urine made strongly acidulous with sulphuric acid produces a weakly yellow-colored ether extract. If sodium is added, the ether is colored a more saturated yellow, the same also the alkaline solution.

Upon addition of acids (H Cl or H₂ SO₄) the urine becomes cloudy through separated (free) Dinitronaphthol. No injections made.

March 12—1:00—0.5 through stomach tube.

1:10—Vomiting. Then lively, Normal respiration.

March 13—Diarrhea. Lively. Did, however, eat at noon. Albumen in the urine.

March 14—11 o'clock—1.0 through stomach tube. Trying to vomit. Until 3 o'clock in the afternoon, however, no vomiting.

March 15—Is found dead in the cage. Dissection accidentally neglected.

Experiment II. Dog of 5700 gr.

March 22—1 gr. through tube.

" 23—Was delivered of five living young ones.

" 24-29—Dog and its young ones lively.

That Martius yellow acts poisonous in stomachical application appears from Experiment I, as any another cause of death except the one through poisoning appears to be excluded.

Better proofs, however, are the following experiments in which the color was applied hypodermically.

Experiment III. Dog of 5800 gr.

April 30—10 A. M.—About 0.1 gr. in about 25 water injected hypodermically in several places of the back. Animal lively. In the afternoon diarrhea.

May 1—0.1 Hypodermic injection. } Diarrhæa.

Urine contains considerable albumen. When adding a little acid, a precipitate of free Dinitrophenol is produced. Ether added is colored weakly yellow. Addition of alkali to the separated ether extract colors same and the alkaline solution yellowish brown. It is possible to color wool yellowish brown with the urine made weakly acidulous.

May 3—0.1 hypodermic injection.

May 4—0.15 hypodermic injection. The urine contains much albumen. The wool coloring succeeds very well. This experiment proves that if small doses of Martius yellow are applied hypodermically, albuminuria is produced.

Experiment VI.

Dog of 8800 gr.

April 30—0.1 hypodermic injection.

May 1—0.1 hypodermic injection.

May 2—0,1 hypodermic injection. Animal is exceedingly thirsty.

May 3—0.1 hypodermic injection. Thirst. Very little appetite.

May 4—10 o'clock—0.2 hypodermic injection. Urine dark brown. Contains albumen. Wool coloring successful.

4 P. M.—Six hours after the injection heavy Dyspnœa. Very thirsty.

7 P. M.—Animal completely apathetic. Strongest Dyspnœa.

The animal dies on the night of the 4th-5th of May. Dissection—Venous hyperæmia of the rectum, of the liver, of the spleen, kidneys and lungs. Pneumonia has begun. Intestines and skin not colored.

This experiment is proof beyond contradiction. Only the poison could be the cause of death, as the operation—hypodermic injection—disappears as causa mortis.

The animal received in the course of five days only 0.6 gr. Martius yellow as Na. salt, or only 0.07 gr. per kilo. The poisoning with Martius yellow produces the following symptoms:

Through the stomach it produces vomiting. The animals become very thirsty and develop high fever with pronounced Dyspnæa. After the first dose already appears albuminuria. The animals die and as it appears mostly asphyctic.

If the substance is brought directly into the blood (Cazeneuve & Lepine) or if it is injected under the skin, the same symptoms, with the exception of vomiting, are observed.

The Martius yellow, therefore, belongs to the harmful colors. As coloring matter for food and liquid

products at least it ought to be prohibited. For coloring of fabrics which come in contact with the skin, its use is not advisable, as the same might prove harmful and dangerous to a scratch of the skin, even if it should only be very slight.

The experiments in which the animals died or became sick when they received an injection of Martius yellow either in the blood or under the skin prove this absolutely.

The fed Martius yellow is at least partly expelled unchanged through the urine.

The wool coloring produced with the urine of the dog—presumably through admixture of the color of the urine—a somewhat darker shade than could be expected of the pure Martius yellow.

4. Naphthol Yellow S.

C₁₀ H₄ N₂ O₈ S Na₂

Naphthol Yellow S also called Acid Yellow S, fast yellow, aniline yellow, Succinine, sulphur yellow, Citronine, Jaune nouveau, Jaune solide, is the calcium salt (natron or ammon.) of the Dinitro-a-naphthol sulpho acid.

1. Dusted in concentrated sulphuric acid appears greenish yellow. The solution in sulphuric acid remains clear if diluted with water. Ether added to this solution remains colorless even upon addition of alkali, because the free color is insoluble in ether. Through this ether experiment Martius yellow which, on account of its cheapness is occasionally mixed with the Naphthol yellow S, can be easily determined.

- 2. The watery solution is not precipitated through muriatic acid.
- 3. The watery solution does not produce a precipitate with liquor sodæ.
- 4. As in all nitro colored stuffs—cyanide of potassium produces a color resembling Isopurpuric acid.
- 5. The watery solution even when diluted considerably is precipitated by ammoniacal copper solution. The solution of the crystalline precipitate in hot water remains clear upon addition of strong muriatic acid, and does not impart anything to ether.
- 6. Muriatic acid solution of stannous chloride creates upon addition of:
 - a. Ammonia, orange coloring.
 - b. Ferric chloride, red coloring.
- 7. Ferric chloride produces a Burgundy red precipipate which is partly dissolved when heated; reappears, however, when cooled off.

Used in place of Picric acid for coloring of wool and silk and for printing of textile fibers. Also for coloring of food products?

Animal Tests.

Cazaneuve and Lepine gave daily to a dog of 15 kilos during 14 days 0.5 gr. Naphthol yellow S, then for ten days daily 2 gr. each and finally for 10 days 4 gr. each. The animal was delivered of nine young ones. Eight of them lived. No disturbance whatsoever was observed on the animal used for this experiment. The urine was free of albumen. Several

times the color solution was injected directly into the blood. No symptoms of poisoning could be observed.

2 to 4 gr. of the coloring (per kilo) produced in the human being colics and diarrhœa.

The above named authorities consider the coloring matter as non-poisonous and as a weak purgative.

Cazeneuve and Lepine curiously pronounce the naphthol yellow (Jaune N. S.) used by them especially hard to dissolve, possibly they experimented with a different product.

My own experiments were made on dogs with a preparation for which I am indebted to Dr. C. A. Schulz. Same was purified through extracting and re-crystallizing.

EXPERIMENT I.

Dog of 4800 gr.

- May 7—2 gr. dissolved in water through stomach tube.
 - "
 8—Did eat. Breathes quietly. Consistent almost black fæces. Urine neutral. Free of albumen. The coloring of wool succeeds. 1.75 gr. through stomach tube.
 - "9-10—No albumen in the urine. Animal lively.

 Breathes quietly. Ate well. No injection.
 - " 11th—2 gr. injected. Animal normal. Traces of albumen in the urine (?).
 - " 12th—2 gr. injected. Animal normal. Traces of albumen in the urine. Solid fæces. In spite of the at least considerable dose of 7.75 gr.

in 6 days and 1.6 gr. per kilo animal, no poisoning symptoms with the exception of a very small albuminurie which was probably there before the beginning of the experiment, were observed.

The following experiments to which a female dog and her 3 1/2 weeks' old young one were used show that no poisoning symptoms appeared by hypodermic injection of naphthol yellow S.

EXPERIMENT II.

Dog of 5800 gr.

May 11th—0.2 gr. in about 32 ccm. water hypodermic injection. Animal lively and with good appetite.

May 12th—0.2 gr. hypodermic injection.

" 13th-16th—Animal lively. Desire to eat same as usual. Nurses its young one.

EXPERIMENT III.

3 1/2 weeks' old dog of 1040 gr.

May 11th—0.1 in about 15 water hypodermic injection.

" 12th—0.1 hypodermic injection. Animal lively, also during the following days.

Especially Test III shows that repeated doses of 0.1 per kilo can be endured even by a hypodermic injection by a young animal, without producing any apparent disturbances.

The harmlessness of naphthol yellow S is a still more interesting fact as the same differs from the very poisonous Martius yellow only through a sulpho

group (HSO₃). The HSO₃ group, however, produces the solubility of the color. A soluble color, however, common sense teaches, should be more poisonous than the insoluble color, Martius yellow, from which it was obtained. We are plainly not as yet in a condition to decide about the poisonousness or non-poisonousness of a product except through experiments, no matter how well we know the chemical composition of the product.

5. Brilliant Yellow.

$C_{10} H_5 N_2 O_8 SNa.$

- 1. The aqueous solution colored yellowish brown is turned into a lighter yellow through muriatic acid but is not precipitated. Ether, if added, is colored pale yellow.
- 2. Liquor sodæ produces an orange yellow crystalline precipitate.
- 3. With ferric chloride the solution is colored a dirty yellowish green. In a striking light it is not transparent, almost black. Before the beginning of the dark coloring the solution appears for a short time colored reddish brown.
- 4. Ammoniacal copper solution produces only after some time a crystalline precipitate.
- 5. With stannous chloride and following the addition of ammonia or ferric chloride, furthermore with cyanide of potassium, brilliant yellow acts the same as Martius yellow.

ANIMAL TESTS.

a. Stomachical Application.

Dog of 5650 gr.

- July 26th—Urine contains traces of albumen.
 - " 26th—3 gr. in a little water applied through stomach tube.
- July 27th—Animal lively. Did eat. Urine intensely orange yellow. The coloring of wool through the urine, made weakly acidulous by sulphuric acid, succeeds. Urine contains brilliant yellow and doubtful traces of albumen. Urine mixed with muriatic acid imparts to ether a substance, coloring the ether a faint yellow. Liquor sodæ discolors the ether almost completely, and becomes itself yellow colored.
- July 28th—Animal lively. Did eat. Urine contains very little coloring matter. 3 gr. through tube dissolved in a little peptone.
- July 29th—Animal very lively. Urine almost free of albumen. Contains a great deal of coloring matter. Wool coloring succeeds well.
- July 30th—2.5 gr. in a little peptone solution through tube. Urine alkaline. Almost free of albumen. Animal lively. Did eat. Coloring of wool in the urine, to which sulphuric acid was added, succeeds well.
- July 31st—3 gr. through tube in a little peptone solution.
- August 5th—Dog completely normal. Gained about 180 gr. during the experimental period. The existence of the brilliant yellow in the urine was

proven besides, through the coloring of the wool in the sulphuric acid bath, in the following manner: The urine is made acidulous with muriatic acid and shaken with ether. The ether extract imparts the coloring matter, liquor sodæ, which is identified by the above described reaction.

b. Hypodermic Injection.

Dog of 11600 gr.

July 27th—Urine free of albumen and sugar.

" 28th—0.2 gr. brilliant yellow, suspended in about 10 ccm. water.

July 29th—Urine in thin layers intensely orange yellow; in thicker layers orange red, but free of blood and albumen. Animal lively. Did eat.

July 30th—0.3 gr. hypodermic injection. Animal lively. Did eat. Urine contains a little albumen.

July 31st—No urine. Animal lively. Did eat.

August 5th—Dog is lively. Its urine contains very little albumen. It gained almost 300 gr. during the experimental period.

I regret that I have no material for further animal experiments.

The brilliant yellow applied through the stomach is surely not poisonous, even in large doses.

The dog which received the coloring matter in, comparatively speaking, large quantities through hypodermic injections, was still completely lively for eight days after the last injection, and with good appetite. The secretion of albumen during the applications

remained exceedingly minimal. In brilliant yellow, the same as in naphthol yellow S, the ability of the sulpho group (H SO₃) to make the product non-poisonous is apparent.

6. Aurantia.

C₁₂ H₈ N₈ O₁₂.

Aurantia or Kaiser yellow is the ammonium or the sodium salt of the Hexamitrodiphenylamin.

- 1. Dusted in concentrated sulphuric acid is faintly yellow, addition of water produces flaky precipitate.
- 2. Solutions of aurantia are precipitated by strong muriatic acid, at the same time discharging the free color acids. Ether dissolves the precipitate with yellow color. If an alkali is added to ether it is discolored, the alkali is colored yellowish brown, almost red.
 - 3. No precipitate is produced through liquor sodæ.
- 4. Ammoniacal copper solution produces a vermilion red precipitate. When treated with fuming muriatic acid this produces a precipitate which acts the same with ether as described above under No. 2.
- 5. With cyanide of potassium, with muriatic solution of stannous chloride, and with later addition of ammonia or ferric chloride, aurantia acts the same as nitro colors. Compare, however, picric acid.
- 6. Ferric chloride produces a chamois colored precipitate. It is used for orange coloring of wool, silk and especially leather.

The poisonousness of aurantia has been repeatedly asserted and disputed.

According to Gnehm, the preparation of Bindschelder and Busch, is poisonous. It produces blisters with considerable swelling upon the hands and arms of the workingmen engaged in the production of the color, and also of the dyers who use same.

8. Summary.

The results of the experiments which have been obtained in regard to the effect of nitro colors upon the animal organism warrant the following conclusion:

Only the sulphonized nitro dyes, naphthol yellow and brilliant yellow, are non-poisonous, and may be used for coloring of food and liquid products.

Poisonous, however, are picric acid, Dinitrokresol (Saffronsurrogate) and Martius yellow.

Suspicious, aurantia.

AZO COLORS.

Regarding the influence of some azo colors upon the human system as well as upon animals we are indebted to Cazeneuve & Lepine for some excellent tests which the following table will explain:

-					
	French Description.	Synonyms.	Constitution.	Belongs to Group of	Effects.
	Rouge Soluble.	Azorubin S, Fast Red, C. Carmoisin.	${ m C_{10}}{ m H_{6}}^{a{ m SO_{3}}{ m Na}}_{6a{ m N=N-C_{10}}{ m H_{5}}^{a{ m OH}}_{a{ m SO_{3}Na}}$	Mona- zo colors	Non-poison- ous also for the human being.
	Rouge Pourpre.	Brilliant- Ponceau, Cochineal Red or Fast Red D., Bordeaux	${ m C_{10}^{}}^{ m H}{ m aSO_3^{}}{ m Na} { m C_{10}^{}}^{ m H}{ m aSO_3^{}}{ m Na)_2} { m N. BCaze neuve does not state which B-Naphthol-disulpho acid was used for the production of color.}$		do.
	Bordeaux B.	Fast Red B,	$\mathbf{C}_{10}\mathbf{H}_{7}a\mathbf{N} = \mathbf{N} - \mathbf{C}_{10}\mathbf{H}_{4}^{\beta \mathrm{OH}}_{4(\mathrm{SO}_{3}^{}\mathrm{Na})_{2}}$	do.	do.
	Ponceau R.	Ponceau 2R, Xylidin Red, Xylidin Ponceau.	${^{\mathrm{C_6H_{^3}\!N=N-C_{_{10}}\!H_{_{4}\!(SO_3^3\!Na)_2}^{\beta\mathrm{OH}}}}}$	do.	Non - poison- ous for dogs through stom- ach and also through blood
	Orange I.	a Naphthol - Orange Tropaeolin 000 No. 1.	$C_6^{H_4^{(4)} SO_3^{Na}}$ Na $C_6^{H_4^{(1)} N=N-C_{10}^{H_6^{(a)}OH}}$	do.	do.
	Jaune Solide.	Fast yellow R, Acid Yellow R, Yellow W.	$(2)CH_{3} \qquad (2) CH_{2} \\ C_{6}H_{3}SO_{3}Na \qquad (1) N-N (1) C_{6}H_{2}SO_{3}Na^{2} \\ (?) \qquad (?) \\ See Eger, Ber. 22,851, 1889.$		For dogs through stomach and through blood harmless. For the human being harmful (?)

The azo colors examined up to now belong, therefore, entirely to the monazo colors, and are all entirely harmless.

1. Bismarck Brown.

 $C_{12}H_{13}N_5$, 2HCl.

Synonyms: Manchester brown, Phenylen brown, Vesuvin, Aniline brown, Leather brown, Cinnamon brown, Canelle, English brown and Gold brown.

A dark brown powder, soluble in water, with a brown color.

The aqueous solution produces:

With muriatic acid a brown precipitate, soluble in water, with a brown color.

With acetic acid, a brown solution, no precipitate.

With liquor sodæ, a brown precipitate, very little soluble in water.

With ammonia, brown precipitate, which is soluble with brown color in excess of ammonia.

With ammoniacal copper solution, brown precipitate hard to dissolve, even in hot water, reappearing in cooling off.

α . FEEDING TESTS.

Dog I—5690 gr.

June 11th—No albumen.

June 12th—No albumen.

June 13th—2 gr. through tube.

10:30—Injection.

12:00—Vomiting.

June 14th—2 gr.

10:00—Injection.

12:00—Vomiting. Did not eat anything.

June 15th—Did not eat anything. Animal moves about very little.

June 16th—2 gr. Two hours after injection violent vomiting.

June 17th-20th—Did not eat anything. Drank only water.

June 21st—Did eat. Livelier. Albumen in urine.

June 22nd—5 gr. Animal vomits ½ hour after injection.

June 23rd-27th—Did hardly eat anything. Albumen in urine.

June 28th—Lively.

June 30th—Did eat. Albumen in the urine.

The animal was watched up to July 15th. In the urine at the last only slight traces of albumen. Appetite as before.

Dog II.—29.5 kilos.

April 29th—Little albumen.

April 30th—5 gr. through tube.

May 1st—Urine brown. Animal lively. Eats as usual.

May 2nd—5 gr. through tube. Bismarck brown can be proven through wool coloring and through chemical reactions in the urine.

May 4th—5 gr. Urine brownish. No albumen.

May 5th—Urine colored normal. No albumen.

May 8th—15 gr. Animal vomited an hour after injection.

May 9th—Did not eat anything. Bismarck brown can be proven in the urine.

May 11th—15 gr. Vomiting one hour after injection.

May 12th—Animal eats little. Seems sick.

May 14th—Animal lively again.

May 15th—15 gr. Vomiting $1\frac{1}{2}$ hours after injection.

May 16th—Did not eat anything. Urine free of albumen.

May 18th—Animal again normal.

May 22nd—Animal normal. Weight, 28.9 kilos.

Experiment III.

Dog of 5.5 kilos received daily during a month 0.25 gr. Bismarck brown with its food. The animal felt well during the whole time. Did not vomit and ate as usual. It gained during the experiment about 350 gr.

b. Hypodermic intra-abdominal injection.

Test VI.

Dog of 6.3 kilo received in the course of 20 days nine injections of 0.1 gr. Bismarck brown in 8 to 10 ccm. sterilized water under the skin of the back. The animal remained absolutely normal. The urine was of normal color and did not contain any albumen.

Test V.

I injected 3 times each 0.1 grain Bismarck brown dissolved in 8 to 10 ccm. sterilized water in the ab-

domen of the same animal. The animal showed a little rise of temperature and did not eat. Urine remained colorless. The dog recuperated completely within eight days.

Bismarck brown produced vomiting and albuminurie when administered through the stomach in dogs in a dose of 0.35 per kilo (Experiment I). Further disturbances did not set in even in large doses (Experiment II). Small doses (0.045 gr. per kilo) proved, even by frequent application (Experiment III), entirely harmless. Hypodermical injections of doses of 0.016 gr. (Test IV) proved harmless. The same doses, however, in abdominal injections produced light disturbances (Test V).

The urine remained colorless in small doses. Only in larger dozes unchanged Bismarck brown could be proven in the urine.

2. Sudan I. C₁₆H₁₉N₉O

Sudan I. was first obtained from C. Lieberman out of the Diazobenzol chloride and β -Naphthol.

In its pure state red crystals. Not soluble in water. Soluble in alcohol with orange red color.

The alcoholic solution produces:

With liquor sodæ, a red brown solution.

With ammoniacal copper solution, a brown precipitate.

With diluted ammonia, same as diluted liquor sodæ.

By dusting in concentrated sulphuric acid, fuchsine red solution which, upon diluting with water, produces an orange yellow sediment.

Dog I.—11.9 kilos.

June 7th—Urine alkaline. No albumen.

June 8th—2 gr. through tube.

June 9th—No injection. Urine of normal coloring. Alkaline. No albumen. Dissolves a great deal of copper oxide in alkaline solution. Considerable sulphates. Distillate of the urine treated with concentrated muriatic acid produces a distinct sediment with bromine water.

June 10th—No injection.

June 11th—2 gr. through tube. Dog lively. Hard fæces.

June 12th—Did vomit. Otherwise lively. Urine is almost free of phenol. 2 gr. through tube.

June 13th—2 gr. through tube. Urine dark brown. Alkaline. Albumen plainly discernible. There are some sulphates.

June 14th—2 gr. through tube. Albumen distinct.

June 15th—2 gr. through tube.

June 16th—Lively. Did eat. Weight 11.55 kilos. Lost 350 gr. in 10 days.

June 22nd—Lively. Urine colored normal. No albumen.

June 23rd—5 gr. through tube. Urine a little darker than normal.

June 24th—Did eat little.

June 25th—5 gr. through tube. Ate little.

June 26th—Through hot alcohol a great deal of unchanged coloring matter can be extracted out of the fæces which is again precipitated in red crystals when the alcohol is cooled off, and shows the

above described re-actions. Very little albumen in the urine.

June 27th—Animal lively. Ate little.

June 29th—Ate well. Urine colorless.

June 30th—Animal lively. Very little albumen in the urine.

The coloring matter is not entirely harmless in the administered doses, as it seems to be capable of producing some albuminurie. Hypodermic injections had to be omitted on account of lack of proper solvents.

3. Metanitrazotin.

Azo coloring matter of Diazo M-Nitraniline and combination with β -Naphthol C_{16} H_3 N_3 O_3 .

The product is hardly soluble in alcohol of 90%. Very hard to dissolve in benzol and in glacial acetic acid. Soluble in warm alcoholic solution of caustic soda and is precipitated after filtration with muriatic acid. The precipitate is washed out with hot water after decanting. The coloring matter presents a red powder.

The alcoholic solution gives:

With liquor sodæ, Burgundy red coloring which is changed into yellow by acids.

With ammonia as with liquor sodæ.

In dusting in concentrated sulphuric acid fuschine red liquid is produced which through diluting with water is colored orange yellow and shows a greenish yellow fluorescence (through a finely distributed sediment?).

Dog I.—12.6 kilos.

July 11th—Traces of albumen in the urine.

July 12th—Same.

July 12th—1 gr. through tube. Urine pale, alkaline. Traces of albumen. Phenol hardly to be proven.

July 13th—2 gr. through tube. Urine plentiful. Pale yellow. Cloudy. Considerably alkaline. By addition of acids to the urine same effervesces considerably. No sugar. Traces of albumen. No phenol.

July 14th—2 gr. through tube. Urine considerably alkaline.

July 15th—2 gr. through tube. Urine very plentiful. July 16th—Dog lively. Weight 12.45. Lost, therefore, 150 gr. within 5 days.

A second dog (5.6 kilos) received 10 doses each one 1 gr. in the course of 20 days. The animal kept well. The urine was free of albumen and colorless. Duration of observation five weeks.

After the experience gained with the nitro coloring matters I had counted upon a poisonous effect of the metanitrazotin. However, in spite of the presence of the nitro group, the color proved non-poisonous.

4. Paranitrazotin.

Azo coloring matter out of Diazo p-Nitraniline and combination with β -Naphtholmonosulpho acid S (Schaeffer) C_{16} H_9 N_3 O_6 S Na.

Reddish brown powder, soluble in water with an orange brown color.

The watery solution gives:

With liquor sodæ fuchsine red solution. With ammonia as with liquor sodæ.

With sulphate of copper no change.

With ammoniacal copper solution, reddish violet sediment, soluble in ammonia with same color.

If dusted in concentrated sulphuric acid a light red solution is produced which is colored orange yellow if diluted with water. The coloring matter, on account of its production, may be called Paranitrazotin.

A rabbit of 1.5 ko. received two doses of 2.5 gr. each through the stomach tube in the course of three days. The animal remained well.

Further experiments could not be undertaken on account of scarcity of substance.

5. Orange II. $C_{16} H_{11} N_2 O_4 S Na.$

Synonyms:—Orange No. 2, β -Naphthol Orange, Tropæolin 000 No. 2, Mandarin, Mandarin G Extra, Chrysaurin, Gold Orange.

Orange red crystals easily soluble in water with orange red color.

The aqueous solution produces:

With muriatic acid, a brown precipitate, which is readily soluble in alcohol with orange red color.

With liquor sodæ, red brown solution.

With ammonia as with liquor sodæ.

With ammoniacal copper solution, gelatinous red brown precipitate.

By dusting in concentrated sulphuric acid, fuschine red solution which produces brownish yellow precipitate if diluted with water.

a. Stomachical Application.

Test I.—Black poodle of 10.5 kilos.

- July 4th—5 gr. through tube. Urine red. Diarrhœa? Vomiting? The red color of the urine fades out when heated with stannous chloride and muriatic acid.
- July 5th—No injection. Urine red through azo coloring material. Vomiting (?).
- July 6th—Urine red.
- July 7th—Urine a little reddish, precipitating considerably.
- July 8th—Urine scarce, sediment considerable.
- July 9th-12th—Urine alkaline, cloudy, contains albumen.
- July 13th—7 gr. through tube.
- July 14th—Urine orange red. Did not eat anything. Diarrhea. No injection.
- July 15th—No injection. Animal ate little. Urine a little reddish.
- July 17th—2 gr. through tube. Did not eat anything. Diarrhea. Urine neutral, a little reddish, very cloudy. Traces of albumen (?).
- July 18th—Animal very weak. Urine orange. Eyes closed by pus.
- July 19th—No injection. Animal miserable.
- July 20th—Great deal of albumen in orange-colored urine. Animal very wretched. 40 degrees in recto.
- July 21st—Stridor in breathing. Cotton becomes orange-colored through urine.
- July 22nd—Animal very weak. Urine orange red.

With NaOH dark red. With acids yellowish. Cotton dyeing succeeded well.

July 23rd—Animal found dead in its cage.

Dissection (July 24th)—Plenty fatty tissues of normal color. Muscles colored normal. Stomach and intestines pale. In the stomach and in the upper parts of the intestines were found many fresh and already cicratizing abscesses. The liver somewhat fatty degenerated. Kidneys pale. Epithelium fatty degenerated. Lungs normal. Heart pale. Large white coagula in the heart. Brains colorless.

Test II.

A white rabbit, of 2.25 kilos, died after administering of three gr. of the coloring matter within twelve hours. Four hours after injection the animal still jumped about lively in the room. Dissection was accidentally frustrated.

b. Hypodermic Injection.

Dog of 4300 gr.

Dec. 12th—0.5 gr. in about 10 ccm. luke warm water injected under the skin of the back (right).

Dec. 12th-14th—Urine alkaline. A little albumen. No sugar. A little orange-colored.

Dec. 15th—No abscess at the place of injection. Lively.
Did eat. 0.25 gr. hypodermic injection (back left).
Urine orange red, acidulous. Traces of albumen.
Wool dyeing in the urine made acidulous with a little sulphuric acid succeeds well.

- Dec. 17th—0.5 hypodermic injection. No abscesses. A little diarrhœa.
- Dec. 18th—T=39.5 degrees in recto. Right eye closed by pus and inflamed. Traces of albumen. Urine colored deep orange. Wool dyeing in urine was successful. No injection.
- Dec. 19th—Catarrh of the eyes is better, but cataract.
 0.5 hypodermic injection. Urine red orange.
 Animal lively. Solid fæces.
- Dec. 20th—No injection. Little albumen. Animal trembles.
- Dec. 21st—Solid fæces. Little albumen in the urine. 0.75 gr. hypodermically injected in two places of the back.
- Dec. 22nd—Dog very wretched. Trembles a great deal and growls. Solid fæces. Little albumen in the urine.
- Dec. 23rd—Status idem.
- Dec. 25th—Abscess in place where injection of December 21st was made.
- Dec. 26th--Livelier.
- Dec. 27th—Abscess opens by itself. Weight 3840 gr. Decrease in 15 days 460 gr.
- Jan. 2/89—Abscess almost healed. Animal lively. Did eat.
- Jan. 3rd—Animal loses its hair.
- Jan. 14th—Animal almost without hair. Weight 3890 gr. Lively. Eats considerably.
- Jan. 17th—Sleeps much. Eats considerably.
- Jan. 26th—Has recuperated completely. Weight 5120 gr.

β-Naphthol orange, as shown by experiment I, is, even in small doses, poisonous through the stomach, and brought about the death of a medium sized dog; as specific may be considered the experiment with the rabbit (II).

In contrast to β -Naphthol orange, Cazeneuve and Lepine found the corresponding α -naphthol orange to consist probably of:

$$N = N - 0H$$

$$HSO_3$$

which varies from β -Naphthol orange only through the position of the Hydroxyl group to be non-poisonous. Even in hypodermic injections the β coloring matter seems to produce poisonous effects. The animal, however, withstood the attack.

6. Ponceau 4 G. B. $C_{16}H_{11}N_2O_4SNa$.

Synonyms—Crocein Orange, Brilliant Orange.

A red powder, if strictly pure, crystalline, which does not dissolve easily in water with a red color.

The watery solution gives: With muriatic acid, a yellowish brown precipitate which dissolves in alcohol easily, with a yellowish red color.

With liquor sodæ, a yellow solution.

With ammonia, same as with liquor sodæ.

With ammoniacal copper solution, a dirty yellowish brown precipitate.

By dusting in concentrated sulphuric acid, orange yellow solution which, if diluted with water, produces a yellowish brown precipitate.

Dyes wool in acid bath orange-yellow.

Dog I.—12.4 kilos.

June 19th—2 gr. in water through tube. Urine rose colored.

June 20th—2 gr. in water. Urine reddish.

June 21st—2 gr. in water. Dog lively. Urine reddish. No blood. No albumen.

June 22nd—2 gr. through tube. Dog lively. Urine alkaline. No albumen. No phenol.

June 23rd—4 gr. through tube. Urine normal colored, alkaline, cloudy. No albumen.

June 24th—Animal lively. Did eat.

June 27th—4 gr. through tube.

June 28th—Urine normal colored. Free of albumen.

In a second experiment a dog of 8.5 kilos received daily during one month one gr. of the coloring matter through tube. Urine remained colorless. The animal was lively. The appetite was not disturbed. The loss of weight—200 gr. in thirty days—cannot be taken into consideration.

This color can therefore be considered as non-poisonous.

7. Orseille Substitute.

 C_{16} H_{11} N_4 O_5 SNa

Synonym:—Naphtion red (old).

A brown paste soluble in water, with a reddish brown color.

The watery solution gives:

With muriatic acid, a bluish red precipitate soluble in water and 96% alcohol, with reddish brown color.

With acetic acid, a reddish brown solution.

With liquor sodæ, bluish red precipitate, which is very little soluble in water; readily soluble in alcohol—with a brownish red color.

With ammonia, brownish red solution.

With ammoniacal copper solution, a dirty red precipitate soluble in hot water.

By dusting in concentrated sulphuric acid fuchsine red solution which precipitates upon addition of water a reddish brown sediment.

Dyes wool in acid bath orseille red.

a. Stomachical Application.

Dec. 24th-26th—Dog of 3810 gr. Urine weakly, alkaline, contains a little albumen. No Mucin.

Dec. 27th—20 cm. Orseille solution (=1.64 gr. coloring matter), with peptone, through tube. Thereafter inclination to vomit. Did not vomit. Urine normal colored, almost clear, weakly alkaline. Traces of albumen. With acids, alkalines and concentrated sulphuric acid no characteristic change.

Dec. 28th—20 ccm. orseille solution (=1.64 gr. coloring matter), with peptone, through tube. Urine as on the 27th. Solid fæces. Lively.

Dec. 29th-No injection.

Dec. 30th—40 ccm. orseille solution (=3.28 gr. coloring matter).

- Dec. 31st—Lively. Did eat. Urine as usual. Weight, 3.980 gr., therefore a gain of 170 gr. within 7 days.
- Jan. 1/89—Urine colorless. A trifle albumen. Plenty of sulphates.
- Jan. 2nd—50 ccm. orseille solution (=4.1 gr. coloring matter), with peptone, through tube. Urine alkaline. Otherwise as before. Colorless.
- Jan. 3rd—Urine dyes filtering paper rose color. Alkaline. Very little albumen. Wool dyeing successful in urine made acidulous. Animal lively. Discontinued.

A second experiment, in which a dog of 4.5 kilos received daily during one month 10 ccm. dye stuff solution (0.82 gr. color), that is in total 30 times 0,8 gr. = 24 gr. coloring matter, took the same course as Experiment 1, only the urine remained colorless.

b. Hypodermic Injection.Dog of 4980 grams.

- Jan. 2nd—Urine colored normal. Very little albumen. 10 ccm. orseille substitute solution hypodermic (=0.82 gr. color).
- Jan. 3rd—Urine reddish. No injection.
- Jan. 4th—Urine reddish. Traces of albumen. 10 ccm. orseille substitute solution hypodermic (=0.82 gr. color) left of back.
- Jan. 5th—Urine reddish. Hardly any albumen. Plenty sulphates. Animal lively. No abscesses. No injection.
- Jan. 6th—No abscesses. Animal lively. Little albumen.

Jan. 8th—Animal normal. Urine colorless. Little albumen.

Jan. 9th—Animal did eat. No abscesses. 20 ccm. injection (=1.64 gr.) in two places of the back.

Jan. 10th—Did not eat anything. Conjunctiva colorless. Urine reddish. Little albumen. No abscesses. No injection.

Jan. 11th—No abscesses. Urine colorless. Little albumen. No injection.

Jan. 12th—Urine colorless. Little albumen.

Jan. 14th—Weight 4950 gr. No loss of weight within twelve days. Lively. No abscesses.

Jan. 17th—Lively. Very little albumen.

This coloring matter cannot be considered as poisonous in the described doses, neither through the stomach nor if injected hypodermically even though it contains a nitro group. Probably the effect of the NO₂-group has been modified through the also present HSO₃-group, similar as in Naphthol Yellow S.

8. Chrysoidin.

$C_{12}H_{12}N_4HCl.$

The watery solution produces:

With muriatic acid, a gelatinous brown precipitate easily soluble in water with an orange brown color.

With acetic acid, no change.

With liquor sodæ, orange brown precipitate which is hardly soluble in water, readily soluble in alcohol with an orange yellow color.

With ammonia, same as with liquor sodæ.

With ammoniacal copper solution, a brownish red

precipitate soluble in hot water, insoluble in alcohol. By dusting in concentrated sulphuric acid, yellowish brown solution which becomes ponceau colored when diluted with water.

a. Stomachical Application.

March 24th-25th—Dog of 26.6 kilos. Urine not colored. Contains distinct albumen.

March 25th-26th-3 gr. through tube.

March 26th-27th-Urine colored considerably orange brown. Urine contains distinct albumen.

March 29th-30th—Urine little colored. Animal lively. April 1st—10 gr. through tube.

April 2nd-5th—Urine colored deep brown. Little albumen.

April 6th-7th-10 gr. Chrysoidin. Animal did eat. Did not vomit.

April 8th-10th-Urine dark brown. Distinct albumen.

In a second experiment a dog of 9.5 kilos received during one month daily one gr. of Chrysoidin through tube. The animal remained lively. Urine was colorless and almost free of albumen. It lost during this time 1.2 kilos, about one-eighth the total weight.

b. Hypodermic Injection.

April 12th—Dog of 5.85 kilos. Urine not colored. Traces of albumen.

April 13th-14th-0.1 hypodermic in 10 ccm. sterilized water.

April 15th-27th—Urine not colored. Little albumen. Animal lively. Eats as usual.

April 29th-30th—0.1 hypodermic injection.

May 2nd-3d—Animal lively. Urine not colored.

May 5th—Urine not colored. Very little albumen.

May 8th—0.1 hypodermic injection.

May 10th—Urine normal. No abscesses. Ate well. Weight 4.620 gr. Loss 1.230 gr. This is more than $\frac{1}{5}$ of the total weight.

May 15th—Animal normal. Eats a great deal. Urine almost free of albumen.

c. Injection into the Abdomen.

A dog of 4.5 kilos received three times in the course of 10 days, 0.1 Chrysoidin in sterilized water by means of a sterilized syringe injected into the abdomen.

The urine remained colorless but contained a little albumen. The animal was still very lively more than three weeks after the end of the test and kept up a good appetite.

The chrysoidin effects, as my tests show, a little albuminurie and causes a considerable loss of weight. Further disturbances were not observed. After large doses were applied to the stomach a part of the coloring matter was taken up by the urine.

Contrary to the experiments made with the dog, Blaschko describes a repeated recidivating eczema of a laborer engaged in the production of chrysoidin. Whether this skin disease was really produced through the chrysoidin or rather through the different materials used for its production—especially Metaphenylendiamin seems suspicious—needs, I believe, further proofs.

$9.\ Diphenylamine\ Orange.$

C₁₈H₁₄N O₃SNa.

Synonyms: — Acid yellow D., diphenyl orange, orange IV., tropæolin 00, orange B., Jaune d'aniline, helioxanthin (?) orange G. S., new yellow.

Orange yellow powder not very easily soluble in cold water with orange red color.

The watery solution yields:

With muriatic acid, a reddish violet precipitate which is very little soluble in water producing violet solution, the precipitate is easily soluble in 96% alcohol with orange red color.

With liquor sodæ, egg yellow precipitate which is hardly soluble in water with egg yellow color; soluble in 96% alcohol with orange red color.

With ammonia, orange yellow precipitate, which is readily soluble in an excess of ammonia.

With ammoniacal copper solution, yellow precipitate, which is soluble in hot water with a brown color, which, however, is precipitated again when cooling off.

By dusting in concentrated sulphuriic acid, a bluish violet solution which produces a violet sediment when diluted with water. This sediment is soluble in an excess of water with a reddish violet color.

Dyes wool orange yellow in the acid bath. Serves as an indicator in titrating, as it is colored red through a little free acid (not through carbonic acid).

a. Stomachical Application.

Test I.

Jan. 16-18th—Dog of 27.35 kilos. Little albumen. Jan. 19th —5 gr. in peptone through tube. Urine, if allowed to stand, becomes dark colored from top downwards. Contains albumen. Considerable sulphates. Alkaline. Lively. Did eat.

Jan. 20th—Urine almost black. Otherwise as on the 19th.

- Jan. 21st—5 gr. Urine alkaline. Almost black. The urine distilled with strong muriatic acid shows only traces of phenol. The genuine urine shows with ferric chloride no characteristic change. If treated with strong muriatic acid a flaky precipitate is produced which is not soluble in water, but soluble in hot alcohol. The filtrate of the urine precipitated with acid shows the distinct reactions of albumen.
- Jan. 23d—The precipitate produced through acid has disappeared out of the urine. Plenty of albumen. 3 gr.
- Jan. 24th—Precipitate produced by muriatic acid is missing. Urine almost colorless. Little albumen.
- Jan. 25th—Urine very dark colored; produces precipitate with muriatic acid. Little albumen.
- Jan. 26th—Urine colorless. Little albumen.
- Jan. 27—Same as on the 26th.
- Jan. 28th—10 gr. Considerable urine, almost black. Same contains much albumen and considerable sulphates. Alkaline.
- Jan. 29th-30th—Urine colored dark. Much albumen. Has eaten little.
- Jan. 31st—Plenty of albumen. Weight 26.35 kilos; therefore a loss of 1 kilo; that is, 1/27 part of the weight within 14 days.

- Feb. 2d—15 gr. Urine colored deep black. Plenty albumen. Animal lively.
- Feb. 3d—Urine dark brown. Distinct traces of albumen. Did eat well.
- Feb. 7th—Urine almost normal colored. Animal lively.

Test II.

- Jan. 15th-18th—Dog of 9730 gr. Little albumen.
 - "19th—3 gr. in peptone.
 - " 21st—3 gr.
 - " 22d—No injection. Animal lively.
 - " 23d—2 gr. Did eat.
 - " 27th—Lively. Did eat. 3 gr. color.
 - "28th-30th—Each 3 gr. color. Animal lively.
 - " 31st—3 gr. color. Animal did eat. Lively. Weight 9820 gr.

The animal receives from February 2d to 15th daily three gr. coloring matter. In the urine unchanged coloring matter and albumen. Animal remains lively.

b. Hypodermic Injection.

Test III.

- March 20th—Dog of 5450 gr. Distinct albumen in the urine.
- March 21st-22d—Urine colorless. Contains distinct traces of albumen. 0.1 hypodermically.
- March 22d-23d—No abcess. Urine colorless. Animal lively.
- March 23d-24th—0.1 hypodermically. No abscess. Urine colorless. Little albumen.

March 25th-26th—Urine colorless. Little albumen. No change with muriatic acid or liquor sodæ.

March 26th-27th-No abscess. Did eat.

March 29th-30th—No abscess. Urine colorless.

March 31st-April 4th—Did eat. 0.1 hypodermic.

April 4th—Lively. No abscess. Weight of the body 5220 gr.; therefore. a loss of 230 gr.; that is, 1/24 of the total weight in 14 days.

April 12th—No abscess. Lively.

The Diphenylamine orange therefore produces albuminurie, according to above tests. Further disturbances did not appear after observation of the animals used for the tests during several weeks.

10. Metanil Yellow.

 $C_{18}H_{14}N_3O_3SNa.$

The coloring matter, a yellowish brown powder, smells strongly after diphenylamine.

The aqueous yellow-colored solution produces with muriatic acid a violet precipitate which is gradually dissolved by an excess of muriatic acid or water into a fuchsine red liquid. Liquor sodæ does not change the watery solution at first. After a little while, however, a yellow crystalline precipitate is produced which is soluble in warm water with an orange red color.

By dusting in concentrated sulphuric acid a violet solution is produced, which becomes colored fuchsine red if diluted with water.

With ammoniacal copper solution a heavy, other yellow, flaky precipitate is produced, which is very hard to dissolve in water.

For purifying purposes the coloring matter was dissolved in water, filtered and extracted by sodium acetate. After drawing off the yellow material is obtained in the shape of yellow crystals out of the hot alcohol in which it is hardly soluble at all. The coloring matter used for the physiological experiments was almost pure, as is proven by the following analysis:

0.4895 gr. of coloring matter dry at 105 degrees yielded 0.084 $\mathrm{Na_2}$ $\mathrm{SO_4}$

Na Brown. Colored. 5.6

Same as Diphenylamine orange dyes wool orange yellow in the acid bath.

a. Stomachical Application.

Test I.

April 2nd—Dog of 11.600 gr. Urine almost free of albumen.

April 4th-5th-10 gr. Metanil yellow through tube. Animal vomited and did not eat anything.

April 5th-6th-10 gr. metanil yellow. Did vomit and did not eat anything.

April 7th—Animal is very miserable. Did not eat anything. Respiration difficult.

April 8th—Died during the night of 7th-8th.

Dissection:—Stiff. Outer skin not colored. Mucous membranes yellowish. Intestines pale, not colored. Kidneys pale, not colored. Liver red, contains a great deal of unchanged coloring matter, as it is colored red with concentrated sulphuric acid. In the stomach a great deal of un-

changed coloring matter. In the otherwise normal lungs a circumscribed focus in which tuberculosis bacilli can be proven. The deposit was found on the front part of the lower right lobe of the lung.

The animal received in the course of 4 days 20 gr. of coloring matter, that is, 1.7 per kilo and was killed by this dose.

Test II.

- March 19th-20th—Animal of 11.25 kilos. Distinct traces of albumen.
- March 20th-21st—1 gr. Urine colorless. Distinct traces of albumen.
- March 22nd-23rd—Urine colorless. Becomes colored dark from the top downwards. Distinct traces of albumen.
- March 24th-25th—Urine orange yellow in thin layers. With muriatic acid bluish violet. With liquor sodæ orange red. Animal lively. Conjunctiva not colored.
- March 25th-26th-10 gr. Dog vomited considerably about one hour after injection.
- March 26th-27th—Ate little. Urine dirty greenish yellow.
- March 28th-29th—Urine colored normal. Distinct traces of albumen.
- April 1st—5 gr. Animal ate very little. Died during the night of 1st-2nd of April. 8750 gr.

Dissection:—Skin and subcutaneous cellular tissue, serose, intestines, contents of intestines yellow colored (metanil yellow). Contents of the intestines were

colored ruby red with concentrated sulphuric acid, contained therefore unchanged coloring matter. Liver very rich on blood, colored dark red, re-action with concentrated sulphuric acid. Kidneys colored deep yellow. Conjunctiva yellow. Urine of the bladder orange yellow, becomes red through concentrated sulphuric acid, therefore contains unchanged coloring matter.

The dog received in the course of 12 days 21 gr. of coloring matter, therefore 0.53 gr. per kilo. This dose proved fatal.

b. Hypodermic Injection.

Test III.

Dog of 5220 gr.

April 3rd-4th—Traces of albumen in the urine.

" 5th-6th—0.1 gr. in 10 ccm. sterilized water hypodermically. Animal trembles a great deal.

April 7th—Urine uncolored. No abscess. Animal trembles.

April 9th—0.15 gr. hypodermic injection in two places. Animal trembles, eats a great deal.

April 11th—0.15 gr. hypodermically. No abscess.

Animal livelier, no more trembling observed.

Urine not colored. Contains traces of albumen.

April 14th—4790 gr. Animal lively. Did eat.

In accordance with tests I and II the metanil yellow must therefore be considered poisonous through the stomach. The dosis lethalis proves to be 0.53 gr. according to test II.

The isomeric diphenylamine orange, however, is non-poisonous.

11. Azarin S.

Yellowish orange colored thin paste. It smells after sulphuric acid and shows strong acid reaction. Not completely soluble in water.

The watery solution yields: by heating with muriatic acid a yellow precipitate which is soluble in alcohol with a yellow color.

With ammonia, brownish red solution.

With liquor sodæ, bluish violet solution which becomes reddish violet colored when heated and retains this color when cooling off.

With concentrated sulphuric acid, dark, red solution, at the same time the sulphurous acid escapes. In diluting the red solution with water, a brown precipitate is produced, which is readily soluble in alcohol with brown color.

With ammoniacal copper solution, violet precipitate; in thin layers this precipitate appears red.

a. Stomachical Application.

A large dog of 25.6 kilos received in the course of 25 days 35 gr. Azarin suspended in water through the tube. The urine was colored faintly yellow and contained distinct traces of albumen; when heating same with muriatic acid, sulphurous acid was developed. The appetite of the dog was not diminished.

In a second experiment a dog of 10.3 kilos received in the course of 20 days 20 gr. Azarin S. which were given him through the tube. Urine as in Test I. The animal remained lively.

b. Hypodermic Injection and Injection into the Abdomen.

A dog of 4.7 kilos received injected under the skin of the back three times in the course of eight days, each time 0.1 gr. azarin paste mixed with 10 ccm. water. No abscesses appeared during the time of the observation (three weeks). No albumen. No strange coloring matter in the urine. Appetite undisturbed.

Into the abdomen of another dog were injected with Koch's sterilized syringe on May 16th about 5 ccm. azarin paste dissolved in about 5 ccm. sterilized water—in total therefore about 10 ccm. liquid. The following day the animal did not eat anything. The urine remained colorless. On the third day the animal appeared to be very miserable. Did not eat anything. Trifle albumen in the urine. The following day the dog is found dead in its cage.

Dissection.—Peritoneum and the surface of the intestines are covered with red flakes of a coloring matter. The small intestine considerably inter-grown with the peritoneum.

Diagnosis.—Peritonitis, adhæsive, sicca.

This product of the dissection is of considerable interest. The red flakes consisted, as the chemical analysis proved, of the azo coloring matter which is the foundation of azarin S.; therefore the same process took place in the peritoneal cavity which takes place in flxing azarin on the tissue.

Through the stomach azarin S. is harmless.

2. DISAZO COLORS.

The Disazo coloring matters examined by me are classed in the following table:

g No.	Commercial Name.	PRODUCTION.		Group of the	
Running		Diazotized Base.	Combined With.	Disazo Colors.	Effects.
1	Fast Brown G.	2 mol. Sul- fanil Acid.	a-Naphthol.	Primary.	Harmless.
2	Wool Black.	Amidoazo- benzoldi- sulpho acid.	p-Tolyl β-Naphty- lamin.	Secondary.	Harmless.
3	Naphthol Black P.	Amidoazo- naphtalindi- sulpho acid.	β-Naphthol- disulpho acid R.	do.	Harmless through the stomach, harmful in hypoderm c injections.
4	Congo.	Benzidin.	1 mol. m. Amidoben- zolsulpho acid 1 mol. Naphtion acid.	Congo group	Harmless.
5	Azo Blue.	o-Tolidin.	2 mol. a- Naphtolmo- nosulpho acid N. W.	do.	Harmless.
6	Chrysamin R.	o-Tolidin.	2 mol. Sali- cylic acid.	do.	Harmless.

1. FAST BROWN G.

C₂₂ H₁₄ N₄ O₇ S₂ Na₂

Brown powder soluble in water with reddish brown color.

The watery solution yields: With strong muratic acid, a violet precipitate soluble in excess of muriatic acid with violet color which is soluble in water with a brown color.

With liquor sodæ, cherry red solution.

With ammonia as with liquor sodæ.

With ammoniacal copper solution, only in concentrated solution a precipitate which is readily soluble in water with cherry red color.

Dusted in concentrated sulphuric acid, a reddish violet solution which becomes brownish yellow colored when boiling. The reddish violet solution in concentrated sulphuric acid is colored cherry red when diluted with water.

a Stomachical Application.

Test I.

Jan. 15th-18th—Dog of 9.630 gr. Urine contains very little albumen.

Jan. 19th—3 gr. of fast brown through tube.

" 20th—Little albumen. Almost normal colored. Is colored bluish red with NaOH, therefore must contain traces of the applied coloring matter. The urine acidified with acetic acid dyes wool reddish brown.

Jan. 21st—3 gr.

" 22d—Diarrhœa. Urine red, free of blood, little albumen, with NaOH bluish red. The dyeing of wool with the urine acidified with acetic acid succeeds very well.

Jan. 23d—Urine faintly colored, with NaOH faintly bluish red. 2 gr.

Jan. 24th—Urine deeply red-colored. Little albumen.

- " 25th—Traces of albumen. Urine colorless.
- " 26th-29th-Urine colorless. Very little albumen.
- " 30th—Almost free of albumen. 5 gr. color.
- " 31st—Considerable diarrhœa. Urine hardly colored, turns faintly fuchsine red with NaOH. Little albumen. Weight, 8.820 gr.

Feb. 3d-10 gr. color.

- "4th—Heavy Diarrhœa. Urine contains unchanged fast brown G. Did not eat.
- Feb. 5th—Urine as on the day before.
 - "7th—Urine colorless. Very little albumen. Diarrhœa. Did eat a little.
- Feb. 12th—Animal normal. Little albumen in the urine.

In a second test a dog of 5.6 kilos received daily for one month 2 gr. fast brown G. After the sixth dose light diarrhœa set in which continued almost throughout the entire month. The desire for eating decreased. Loss of weight about 1/5 of the total weight.

According to these tests the coloring matter produces diarrhoa in continued applications even in small doses (Test II), and in less frequent applications in larger doses (Test I) loss of appetite. Weight decreased.

b Hypodermic Injection.

March 1st-3d—Weight 6730 gr.

- " 3d-4th—No albumen.
- "4th-5th-0.1 gr. hypodermic injection in 10 ccm. lukewarm water. Urine not colored. Little albumen.

March 5th-6th—No abscess. Urine colorless. No albumen.

March 6th-7th-No abscesses. 0.1 hypodermic.

" 7th-8th—Colorless. No abscess. No albumen.

March 7th-11th—As on the 7th-8th.

- " 11th-12th-0.1 hypodermic.
- " 12th-13th—No abscess.
- " 13th-14th—0.1 hypodermic. Animal continues to be lively. Did eat.

March 14th-18th—No abscesses. Urine colorless. Little albumen.

March 20th—Animal lively. Weight 6450 gr.

- " 23d—No abscess.
- " 24th-25th—No abscess. Urine almost colorless. Little albumen. No change with NaOH or muriatic acid.

March 25th-26th-0.1 hypodermic.

" 28th—Animal lively. Discontinued.

April 10th—No abscesses. Animal lively.

The health of the animal was not impaired through repeated doses of 0.1 gr. coloring matter injected hypodermically.

2. WOOL BLACK.

$C_{29} H_{21} N_5 O_6 S_2 Na_2$

Black blue powder soluble in water with bluish violet color. The watery solution yields: With muriatic acid, reddish violet precipitate which is soluble in water with the same color.

With liquor sodæ, violet precipitate which is readily soluble in water with the same color.

With ammonia, bluish violet solution.

With ammoniacal copper solution, bluish violet precipitate, which is very little soluble in water.

By dusting in concentrated sulphuric acid, a blue solution is produced, which, when diluted with water, produces a brown precipitate, which is decomposed through boiling.

Through boiling with diluted sulphuric acid, wool black is decomposed (according to Witt) into Tolunaphtazine and Amidoazobenzoldisulpho acid.

Wool black dyes wool bluish black in the acid bath.

a. Stomachical Application.

Test I.—Dog of 29.94 ko.

- Dec. 26-27—Urine a little alkaline. Contains some albumen.
- Dec. 28th—5 gr. of wool black in peptone through tube. Urine of normal color, neutral, contains a little albumen, considerable sulphates, shows with acids, alkalines (even at a boiling point), concentrated sulphuric acid, ferric chloride, no characteristic changes.
- Dec. 29th—5 gr. wool black. Lively. Fæces black. Urine normal colored.
- Dec. 30th—5 gr. wool black. Lively. Urine normal colored. Albumen and sulphates as before. Fæces, black, hard.
- Dec. 31st until Jan. 1st, 1889—Urine not colored.
- Jan. 2nd—10 gr. of wool black through tube. Urine intensely dark blue, in thick layer black, dyes wool blue black in acid bath. Urine contains

albumen. Examined as to albumen after extracting of the dye acid and filtering.

Jan. 4th—Urine colorless. Fæces blue. Little albumen in the urine. 10 gr. of wool black.

Jan. 5th—Urine intensely dark blue, in thick layer almost black. The coloring matter can be extracted from the urine through sodium acetate.

Jan. 6th-7th—Animal did eat. Urine colorless, becomes dark from top downwards when standing. Alkaline. Albumen distinct. Sulphates plentiful. Fæces normal colored.

Jan. 7th-12th—Animal lively.

Jan. 13th-19th—Urine distinctly contains albumen. Animal lively. Eats well.

Jan. 20th—Animal lively. Little albumen in the urine.

b. Hypodermic Injection.

Test II.—Dog of 3520 gr.

Jan. 20th—Urine colorless. Free of albumen.

Jan. 21st—0.25 gr. wool black in 10 ccm. lukewarm water injected under the skin of the back.

Jan. 22nd—Temperature 39.5 in recto. Urine colorless. No abscess. Lively. Did eat.

Jan. 23rd—0.25 gr. Lively. No abscess.

Jan. 24th—0.25 gr. Urine not colored. Traces of albumen.

Jan. 26th–27th—Urine colorless. Temperature normal.

Jan. 28th—Abscess on right half of the back. 0.25 gr. hypodermic.

Jan. 29th—Urine colorless. Little albumen.

Jan. 30th—Urine colorless. Alkaline. Little albumen. Abscess has become smaller.

Wool black is non-poisonous in stomachical application as well as in hypodermic injection.

3. NAPHTHOL BLACK P.

C₃₀ H₁₆ N₄ O₁₃ S₄ Na₄.

Bluish black powder soluble in water with dark bluish violet color. The watery solution yields:

With muriatic acid, a bluish violet solution.

With acetic acid, same as with muriatic acid.

With liquor sodæ, same as with muriatic acid.

With ammonia, same as with muriatic acid.

With ammoniacal copper solution, fuchsine red solution. No precipitate.

With copper sulphate, as with ammoniacal copper solution.

With barium chloride, bluish violet precipitate which is hard to dissolve in water.

With ferric chloride, same as with barium chloride.

By dusting in concentrated sulphuric acid dirty green solution which is colored blue upon addition of water.

a. Stomachical Application.

Test I.

March 1st-2nd—Dog of 26.73 kilos. Urine contains little albumen.

March 2nd-3rd—3 gr. through tube. Urine almost colorless. Little albumen. With NaOH hardly changed. Neither with muriatic acid.

- March 4th-5th—3 gr. through tube. Distinct albumen. Urine colorless. Fæces colored blue.
- March 5th-6th-5 gr. Urine colored weakly reddish violet, becomes colored fuchsine through HCl. Little albumen.
- March 6th-8th—Urine colorless. Little albumen. Animal lively. Did eat a great deal.
- March 9th-10th—Urine dirty bluish red. Is colored orange red with HCl. With NaOH bluish red. Dyeing of wool with the acidified urine succeeds.
- March 11th-12th—10 gr. through tube. Animal did eat. Urine and fæces blue.
- March 12th-13th-Urine as above. Little albumen.
- March 13-14th—20 gr. Quite some albumen. Animal lively. Did eat.
- March 14th-15th-Urine bluish. Distinct albumen.
- March 15th-16th—Urine almost colorless. Distinct albumen.
- March 18th–19th—Urine colorless. Little albumen.
- March 20th-21st-Weight 26.62 kilos.

A second dog (4.5 kilo) received daily during one month one gr. of Naphthol black through tube. Remained completely lively and retained its good appetite.

b. Hypodermic Injection.

Test III.

March 1st—Dog of 3200 gr.

March 2nd-3rd—Urine colorless. No albumen.

March 3rd-4th—Urine as above.

March 4th-5th-0.1 hypodermic in 10 ccm. lukewarm

water injected under the skin of the back (right side).

March 5th-6th—Urine scarce. Colorless. No albumen. No abscess.

March 6th-7th-0.1 hypodermic. Animal ate little. March 7th-8th-No abscess. Urine colorless. No albumen. Did not eat anything.

March 8th-9th—Died during the night of 8th-9th. Weight 2550 gr.

Dissection.—No abscesses. No hardening of the places where the injections were made. Under the skin near the places where the injections were made a great deal unchanged coloring matter. Free of microorganisms. Gelatine plates which were inoculated with the coloring matter taken out of the injection places remained sterilized during nine days. Corpse not yet stiff. Very lean. Mucous membranes and muscles colored normal. Intestines very pale. Mesentery considerably reddened. Liver, spleen, kidneys, lungs strongly hyperæmic. Nowheres exudations.

Test IV.

March 9th-10th—Dog of 3860 gr. Animal was used before for other experiments. Very lean.

March 10th-11th—Urine colorless. Little albumen. March 11th-12th—0.1 hypodermic in 10 ccm. water.

March 12th-13—No abscess. Animal miserable. Urine scarce. Almost colorless. With NaOH, acetic acid, and muriatic acid no change in color. Distinct albumen. 0.1 Hypodermic.

March 13th-14th-0.1 hypodermic. Urine colorless. No abscess.

March 14th-16th—Urine colorless. Albumen very distinct. Animal did eat, but is very miserable.

March 17th-19th—No abscesses. Animal very lean. Distinct albumen.

March 20th-21st—Ate a great deal. 3887 gr.

March 25th—Animal very lean. Did eat. Is killed with prussic acid.

Dissection.—The subcutaneous cellular tissue of the back where the injection was made is colored dark bluish red. The muscles show the same color. Liver and the other organs hyperæmic and enlarged. Rectum a little bluish red colored. Conjunctivæ and mucous membranes of the mouth not colored.

This coloring matter is harmless through the stomach but harmful in hypodermic injections.

4. Congo.

C₃₂ H₂₂ N₆ O₆ S₂ Na₂

A red powder. The watery reddish solution yields: With muriatic acid, a blue precipitate which is hardly soluble even in hot water.

With acetic acid, as with muriatic acid.

With liquor sodæ, only in concentrated solution a reddish brown precipitate easily soluble in water.

With ammoniacal copper solution, a gelatinous red precipitate, soluble in excess of water with red color.

By dusting in concentrated sulphuric acid, same is colored blue. If diluted with water a blue precipitate is produced. Dyes cotton and wool red without corrosion.

a. Stomachical Application.

Test I.—Dog of 7300 gr.

- Dec. 14th-17th-Traces of albumen.
- Dec. 18th—2 gr. of congo in peptone through tube.

 Animal lively. Urine colored almost normal.
- Dec. 19th—2 gr. of congo. Urine pale. Weakly alkaline. Traces of albumen. No sugar.
- Dec. 20th—2 gr. congo. Urine colored faintly red.
 Not changed through acids. Yellow through
 NaOH. Little albumen. Hard fæces.
- Dec. 21st—3 gr. congo. Dog lively. Solid fæces. Urine colored a little reddish. The dyeing of cotton in the urine not otherwise prepared succeeds very well. The red colored cotton is colored bluish through acids. Little albumen in the urine.
- Dec. 23rd-26th—Lively. Urine pale red. Contains a reddish sediment. (Congo!).
- Dec. 27th—5 gr. of congo in peptone. Lively. Urine almost colorless. Weakly alkaline. Little albumen.
- Dec. 28th—10 gr. congo. Dyeing of cotton is successful. Little albumen in the urine.
- Dec. 30th—10 gr. of congo. Animal ate little, but lively. Urine little colored. Weak alkaline. Little albumen. Sulphates present. Weight 6980 gr. Decrease 320 gr. in 16 days.
- Dec. 31st—Lively. No injection. Soft pasty fæces. Temporarily discharged.
- Jan. 15th—Animal lively.

A second dog of 4.3 kilos received one gr. congo through tube daily for one month. The dog remained absolutely well.

b. Hypodermic Injection.

Test II.—Dog of 4970 gr.

Jan. 4th—Urine contains traces of albumen.

Jan. 5th—0.25 gr. congo in 10 ccm. water hypodermically injected under the skin of the back, on the right side.

Jan. 6th—Urine hardly colored. Almost free of albumen.

Jan. 7th—0.25 gr. hypodermically injected under the skin of the back, right side. Urine colorless. Alkaline. Little albumen. Animal seems weak.

Jan. 8th—Ate little. Urine colorless. No abscess.

Jan. 9th—Urine colorless. Ate little. 0.25 gr. under the skin of the back, left side. Abscess on the abdomen right side of the centre line.

Urine colorless. Jan. 10th—Ate little. 0.25 gr. hvpodermically injected under the skin of the back, left side. Big abscess right of the linea alba.

Jan. 11—Animal very weak. Urine almost colorless. Contains little albumen. The big abscess on the right side of the abdomen is split. About 15 ccm. of a blood red liquid are extracted in which can be detected fat drops with the naked eye. liquid curdles after 10 minutes. Shows after a proportionate diluting, stripes of Oxyhæmoglobine -but only very weak. Is colored intensely blue with acids. Consists, therefore, for the largest part of completely unchanged not resorbed congo.

With the microscope can be observed fat drops, red blood particles, the latter partly in normal and partly in abnormal shapes, further, also, pus cells. Micro-organisms which, according to Gramm, can endure the coloring, were not found.

- Jan. 12th—Animal very weak and dejected. Weight 4300 gr., showing a decrease of 670 gr. within eight days. Animal dejected and weak.
- Jan. 13th-14th—The abscess opened on Jan. 11th expels voluntarily a red colored liquid in which is contained considerable congo coloring matter (bluing through acids).
- Jan. 15th—The unopened abscess on the left side seems to become resorbed. Temperature 39.5 degrees in recto. 0.25 gr. hypodermic.
- Jan. 16—Animal very miserable. Does not eat. In recto 39.5. Opened abscess seems to close up.
- Jan. 18—Temperature 39.2. Miserable. Eats little.
- Jan. 22d—Ate something. Cranky and miserable. 40.5 degrees in recto.
- Jan. 24th—Weak and cranky. Did eat.
- Jan. 29th—The one abscess opened voluntarily and expelled unchanged coloring matter as well as pus. Animal eats, but is very weak.
- Feb. 5th—Dog is lively again. Did eat. The abscesses on the abdomen were probably abscesses produced directly from the injection places.

According to Tests I and II congo is harmless even in continued application through the stomach. The disturbances which appeared in hypodermic injection (Test III) are probably effected through the invasion of decay organism and would then have no direct connection with the coloring matter.

5. AZO BLUE.

C₃₄ H₂₄ N₄ O₂ Na₂.

Black blue powder quite easily soluble in water with a reddish violet color.

The watery solution yields:

With muriatic acid, a reddish violet precipitate which is easily soluble in water and in alcohol.

With liquor sodæ, a cherry red solution.

With concentrated sulphuric acid, a blue precipitate which is soluble in the excess of sulphuric acid with an indigo blue color.

By dusting in concentrated sulphuric acid indigo blue solution is produced, which becomes cloudy upon addition of water, at the same time precipitating a violet colored sediment. This sediment is soluble in water with violet color. The solution of the color in concentrated sulphuric acid when boiling becomes brown colored under decomposition.

With ammoniacal copper solution, a cherry colored precipitate is produced which is almost insoluble in water.

a. Stomachical Application.

Test I.—Dog of 8450 gr.

Jan. 7th—Urine pale. Colorless. Little albumen.

Jan. 8th—Urine as on the 7th. 2 gr. through tube in peptone.

Jan. 9th—Dog lively. Did eat. Dark colored fæces. Urine colorless. With NaOH temporarily colored greenish. Albumen?

- Jan. 10th—2 gr. through tube. Urine colorless or shining faintly violet. Strong alkaline. Little albumen. With NaOH or NH₃ temporarily greenish. Nothing characteristic with ferric chloride.
- Jan. 11th—5 gr. through tube. Urine colorless. Little albumen. When boiling with concentrated muriatic acid (not with diluted acetic acid) it is colored remarkably bluish black and very dark. It yields to ether a bluish red colored matter. The distillate is free from phenol.
- Jan. 12th—8 gr. azo blue. Urine a little bluish violet. Plentiful. Animal lively. Little albumen. Does not reduce alkaline copper solution.

Jan 13th-14th—No injection. Urine colorless.

Jan. 15th—5 gr. azo blue. Urine colorless.

Jan. 16th—Urine colorless. Little albumen.

Jan. 18th—Urine colorless. Little albumen. 5 gr. of azo blue.

Jan. 20th—Urine colorless. Little albumen. Weight 8490 gr.

Another dog of 4.7 kilos received during one month 1.5 gr. azo blue through tube. The animal remained well and in good appetite. Albumen appeared very sparingly only in the urine.

b. Hypodermic Injection.

Test III.—Dog of 4600 gr.

Jan. 26th-28th-Urine normal.

Jan. 29th—0.20 gr. in 10 ccm. water hypodermically injected. (Left half of the back.)

Jan. 30th—Abscess commencing on left side. 0.20 gr. in 10 ccm water hypodermic injection. (Right half of the back.)

Jan. 31st—Abscess on the left half of the back was opened. It expels a violet gelatinous matter but only a few drops of blood. The expelled coloring material is unchanged azo blue. The pus contains a great many pus kernels and great many putrefaction bacilli. The urine is colorless. Little albumen. Weight 4580 gr.

Feb. 3rd—Dog eats and is livelier.

Feb. 7th—0.20 gr. injected under the skin of the the abdomen with carefully sterilized syringe after the place of the injection was thoroughly disinfected.

Feb. 10th—No abscess. Animal lively.

Feb. 15th—No abscess.

Feb. 24th—Animal lively. No abscess.

Azo blue is harmless through the stomach as well as in hypodermic injections. The disturbances in hypodermic injections could be traced to the invasion of putrefaction bacteria.

6. CHRYSAMIN R.

C₂₈ H₂₀ N₄ O₆ Na₂

A brownish yellow powder soluble in water with a brown color.

The watery solution yields:

With muriatic acid, a gelatinous brown precipitate which is hardly soluble in water, easier soluble in alcohol with a brown color.

With acetic acid, brown flakes.

With liquor sodae, a gelatinous reddish brown sediment which is soluble in water with a reddish brown color.

With ammonia, a reddish brown solution.

With ammoniacal copper solution, a gelatinous red brown coloring which it is very hard to dissolve in water.

By dusting in concentrated sulphuric acid a reddish violet solution is produced, upon addition of water brownish flakes are precipitated.

Dyes cotton yellow in the soap bath.

a. Stomachical Application.

Test I.—Dog of 9230 gr.

- Jan. 2nd—Urine colored normal. Alkaline. Very little albumen. Considerable sulphates.
- Jan. 3rd—5 gr. chrysamin in peptone through tube. Faeces yellowish, thin. Urine alkaline, yellowish. Dyeing of cotton with urine successful. Very little albumen.
- Jan. 4th—5 gr. chrysamin.
- Jan. 5th—Urine yellowish. With NaOH red. Diarrhea. Animal lively. Did eat.
- Jan. 6th-7th—Animal lively. Little diarrhœa. Urine almost colorless. Little albumen. Plenty of sulphates. Alkaline.
- Jan. 7th—1 gr. chrysamin. Urine little colored. Contains distinct albumen.
- Jan. 8th—No injection. Urine little colored. A little albumen.

Jan. 9th—1 gr. chrysamin in peptone. Lively. Fæces yellowish.

Jan. 10th—2 gr. of chrysamin. Dog lively. Runs about freely all day.

Jan. 11th—2 gr. chrysamin. Animal lively.

Jan. 12th—3 gr. chrysamin.

Jan. 13th—Animal lively. Did eat.

Jan. 14th—Weight 9600 gr., therefore 370 gr. gained within 12 days.

Jan. 15th—Lively. 3 gr. chrysamin.

Jan. 16th-20—Little albumen. Lively. Did eat.

In Test II. an animal of 11.3 kilos received in the course of 10 days three doses each of 10 gr. coloring through the tube. The urine was colored yellowish and contained little albumen. The animal was lively even 14 days after the last application.

b. Hypodermic Injection.

Test III.—Dog of 3680 gr.

Jan. 9th—Urine colorless. Traces of albumen.

Jan. 10th—0.25 gr. chrysamin in 10 ccm luke-warm water hypodermically injected. Urine neutral.A little yellowish. Little albumen.

Jan. 11th—Animal does not eat. No abscess. Dyeing of cotton not successful. 0.25 gr. hypodermic.

Jan. 12th—Animal weak. No abscesses. Urine colored a little, also contains little albumen. 0.25 gr. hypodermic.

Jan. 13th—Little albumen.

Jan. 14th—Animal dejected. No injection. 2 abscesses on the back. 40 degrees in recto.

Jan. 15th—0.25 gr. hypodermic. Urine pale yellow. Distinct albumen. Cotton dyeing not successful.

Jan. 16th—No injection. Cranky. 39.5 degrees. Eats little. An abscess on the back opened by itself and discharged a yellow liquid (Chrysamin).

Jan. 17th—Animal cranky. 39.5 degrees in recto. Abscesses as on the 16th.

Jan. 18th—Abscess discharges. Little color.

Jan. 19th–21st—Temperature 39.5 degrees. Cranky. Ate little. A new abscess seems to form.

Jan. 22nd—Eats little.

The abscess split with the knife discharges about 20 ccm of a gelatinous matter which has the color of the injected coloring and in which is found unchanged color. In the discharged matter bacteria could not be proven for a certainty. Such species which stood Gramm's method were positively not present. Great many fat drops, blood only in traces.

Weight 3210 gr.

The color is harmless through the stomach. The abscesses after hypodermic injection can possibly be traced back to invaded putrefaction organisms, although their existence could not be proven with certainty.

III. Conclusions.

1. Among the twenty-three so far examined azo colors only two—namely, metanil yellow and orange II.—showed such effects through the stomach that they can be pronounced poisonous. The dosis lethalis for the dog consisted for Orange II. of less than 1 gr.

per kilo, and for metanil yellow only 0.53 gr. per kilo.

Of the other coloring matters, a few caused vomiting (Bismarck brown), diarrhea (Fast brown, Chrysamin R.), and a great many of them albuminuria of a lighter degree.

The appearances observed in hypodermic injection are doubtful. The produced abscesses were traced back in a few cases (for instance, azo blue) to the invasion of micro-organisms. Naphthol Black P., however, works evidently poisonous in hypodermic injections.

It seems remarkable how slow in some cases the hypodermically injected watery color solutions were absorbed. Congo could be proven (in Test III.) even seven days after the injection, in large quantities. The same was also observed in Chrysamin.

- 2. The tests with the coloring materials from m-Nitraniline+ β -Naphthol, p-Nitraniline+Schaeffer's Salt, p-Nitraniline+Naphthion acid (=Orseille substitute) show that the addition of a nitro group into an azo color does not produce a poisonous color, as the experiments made with the nitro colors would lead us to expect. This harmlessness of the nitro group in the azo coloring, however, is not produced through the presence of a sulpho group, which dis-poisoning influence was also observed in the nitro colors. This conclusion has to be arrived at from the harmlessness of the metanitrazotin (m-Nitraniline+ β -Naphthol), which contains no sulpho group and is non-poisonous in spite of the nitro group.
 - 3. That colors can be poisonous in spite of the

presence of the sulpho group has been proven through the experiments with Orange II. (Sulfanil acid + β -Naphthol), and with metanil yellow (out of m-Amidobenzolsulpho acid+Diphenylamine).

- 4. The poisonousness of Orange II and of metanil yellow can be traced back to their constitution, as two other colors of known constitution, which are closely related to the constitution of the above, proved to be harmless.
- (a) The poisonous metanil yellow corresponds with the non-poisonous Diphenylamine Orange. As the following formulas will show, the difference of the two materials is in the position of the sulpho group to the azo group.

In Diphenylamine orange said groups are contained in para position, in metanil yellow, in meta position. The correctness of these formulas is proven by the fact that metanil yellow is produced through Diazotizing of Meta-Amidobenzolsulpho acid; Diphenylamine Yellow through Diazotizing of Para-Amidobenzolsulpho acid (Sulfanil acid).

(b) With Orange II., which is poisonous, corresponds a second color, the non-poisonous Orange I.

Both materials differ only through the position of the hydroxyl in the Naphthalin.

In Orange I. hydroxyl has the α position, in Orange II. the β position. This results from the production of the colors which are produced in one

case with the help of α Naphtol, in the other case with the help of β Naphtol.

$$\begin{array}{cccc} {\rm C_6H_4^{(4)}\,SO_3\,Na} & {\rm C_6H_4^{(4)}\,SO_3\,Na} \\ {\rm C_7_{10}H_6OH(\it{a})} & {\rm C_6H_4^{(1)}N\!=\!N-\!C_{10}H_6OH(\it{\beta})} \\ {\rm Orange\,\,I.} & {\rm Orange\,\,II.} \\ & (\it{a-Naphthol\,\,Orange}) & (\it{\beta-Naphthol\,\,Orange}) \end{array}$$

Non-poisonous. Poisonous.

Other azo colors, which contain also the balance of β -Naphthol, for instance, Sudan I., Neucoccin, Fast red B., Xylidin red and Azarin S., are absolutely non-poisonous.

The dog urines, discharged after feeding and hypodermic injection of azo colors, were frequently normally colored, and contained the unchanged coloring material only then when very large quantities of coloring material were embodied in the organism. A part of the fed colors is also found in the fæces, principally when the colors fed were not soluble. At any rate, however, a frequently complicated built color molecule is divided in the animal body and changed into uncolored products. I have never been successful so far to produce colored materials out of urines discharged colorless after feeding with azo colors, which could have closer connection with the color molecule fed previously.

In order to show to what degree some of the coal tar colors are harmless, I have made physiological tests with a few of those colors which are especially and frequently used for food products.

Although it was impossible to establish the exact pedigree and thereby the exact age of the animals

employed, I am confident that none of the animals, with the exception of the guinea pigs, were older than two months. (My opinion was shared by people who make the handling of animals their business, and therefore ought to be somewhat competent judges.) I preferred to employ these young animals, as experience in various previous tests had taught me that a fully developed and matured animal will frequently be able to partake of, comparatively speaking, large doses without any apparent bad effects, which doses, however, sufficed to severely injure, frequently even to kill, very young animals of the same class.

TARTRAZINE.*

COOH

Disodium salt of 1-p-sulphoxylphenyl: 3-carboxyl-4-p-sulphoxylphenyl-hydrazono-5-pyrazolon.

Orange yellow powder readily soluble in water

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with a greenish to gold yellow color. The solution in water yields:

With muriatic acid, no change. With liquor sodæ, a more reddish color.

Tartrazine dissolved in sulphuric acid yields an orange yellow solution which is turned yellow upon diluting with water.

TEST I.

Male Dog of 5445 gr., presumably not older than two months.

When received, somewhat sullen. Did not display much appetite during first day (treatment commenced day after received). Suffered of mild diarrhea. Eyes rather dull. Otherwise lively and seemed in fair condition.

- May 17th, 10 A. M.—Injection 0.20 gr. through tube. The color had been previously dissolved in 20 cc. water and a little peptone had been added. Dog ate well about noontime. Was lively and more playful. Mild diarrhea continued; in fact, seemed to have increased somewhat.
- May 18th, 10 A. M.—No injection. Dog lively. Pasty fæces. Good appetite. Weight 5405 gr., a loss of 40 gr. for which I think diarrhea had to account.
- May 19th, 10 A. M.—Injection 0.20 gr. dissolved same as above, through tube. Dog kept lively throughout the day. Displayed good appetite. Solid fæces.

- May 20th, 10 A. M.—No injection. Dog lively. Good appetite.
- May 21st, 10 A. M.—Injection 0.20 gr. Dog lively. Appetite as usual.
- May 22nd—No observation on account of Sunday.
- May 23rd, 10 A. M.—Injection 0.20 gr. dissolved same as above. Dog appeared somewhat sullen but displayed good appetite. Suffered of mild diarrhœa.
- May 24th, 10 A. M.—No injection. Dog is livelier. Appetite fair. Diarrhœa continues but seems to be somewhat decreased.
- May 25th, 10 A. M.—Injection 0.20 gr. dissolved same as before. Dog lively. Very playful. Appetite as usual.
- May 26th, 10 A. M.—No injection. Appetite as usual. Solid fæces. Lively.
- May 27th, 10 A. M.—Injection 0.20 gr. in solution same as before. Appetite as usual. Very lively and playful. Pasty fæces.
- May 28th, 10 A. M.—No injection. Dog lively. Good appetite. Weight 5560 gr. or a gain of 115 gr. in total weight.

Test discontinued.

CURCUMIN.*

Is the sodium salt of Sulphanilacid–azodyphenylamin-sulphoacid.

Orange yellow powder, frequently dark brown powder which gradully bleaches into a golden to

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orange yellow. Readily soluble in water with yellow color.

The watery solution yields:

With muriatic acid, violet-red solution. With little liquor sodæ, no change. With much liquor sodæ, violet-red.

Soluble in sulphuric acid with bluish red color, if diluted with water fuchsine red.

TEST II.

Very young male rabbit of 0.250 ko.

Animal seemed in good condition when received, was lively and displayed considerable appetite (May 16th).

I dissolved the Curcumin applied to the rabbit at the rate of 1 gr. in 25 cc. of water and added some peptone to each dose. The injections were made by means of tube precisely 10 A. M., no food was given to the animal until 10:30 A. M., and previous to same the weight was taken.

May 17th—Injection of 2cc. solution as above. Animal lively. Weight 0.250 ko. Eats well.

May 18th—No injection. Weight 0.255 ko. Eats well.

May 19th—Injection of 2 cc. solution. Animal lively. Weight 0,256 ko. Eats well.

May 20th—No injection. Weight 0.253 ko. Animal lively. Great desire to eat.

May 21st—Injection of 2 cc. solution. Animal lively. Weight 0.261 ko. Desire to eat not diminished.

May 22nd—No observation.

May 23d—Injection of 2 cc. solution. Animal lively. Weight 0.260 ko. Great desire to eat.

May 24th—No injection. Otherwise no change from day before.

May 25th—Injection of 2 cc. solution. Animal lively. Weight, 0.264 ko. Appetite normal.

May 26th—No injection. Animal lively. Weight 0.266 ko. Did not eat as much as usual.

May 27th—Injection of 2 cc. solution. Animal very lively. Weight 0.270 ko. Considerably increased appetite.

May 28th—No injection. Animal lively. Weight 0.273 ko. Appetite as usual. Gain in total weight 23 gr. Discontinued.

CARMOJSIN.*

Sodium salt of Naphtionacid - azo - 1 - naphthol-4-sulpho acid.

Brown powder soluble in water with fuchsine red color.

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The watery solution yields:

With muriatic acid, dark red precipitate.

With liquor sodæ, somewhat more yellowish.

In sulphuric acid, violet solution, upon addition of water fuchsine red.

TEST III.

Guinea pig (male), age unknown, fully developed, weight 0.518 ko. Was very timid in new surroundings, refused food at first, but later in the day commenced to eat a little (May 16th).

The color applied to this animal was dissolved in proportion of 1 gr. in 32 cc. water. Each injection consisted of 4 cc. of above solution through tube. Injections were made at 10 A. M., then the weight of the animal was taken and at 10:30 A. M. the animal received its food.

May 17th—Injection. Animal timid. Weight 0.512 ko. Appetite somewhat increased.

May 18th—No injection. Animal less timid. Weight 0.515 ko. Appetite increasing.

May 19th—Injection. Animal quite lively. Weight 0.515 ko. Appetite very good.

May 20th—No injection. Animal lively. Weight 0.520 ko. Appetite considerable.

May 21st—Injection. Animal sullen. Weight 0.516 ko. Appetite good. Seems very thirsty.

May 22nd—No observation.

May 23rd—Injection. Animal lively. Weight 0.515 ko. Appetite considerable. Drinks less.

May 24th—No injection. Otherwise same as May 23rd. Weight 0.519 ko.

May 25th—Injection. Animal very lively. Weight 05.16 ko. Appetite good.

May 26th—No injection. Otherwise same as May 25th.

May 27th—Injection. Animal lively. Weight 0.516 ko. Appetite good.

May 28th—No injection. Animal lively. Weight 0.517 ko. Appetite considerable. Loss in total weight 1 gr. Discontinued.

PONCEAU 2 R.*

$$N = N \cdot C_6 H_3 (CH_3)_2$$
OH
$$SO_3 Na$$

$$SO_3 Na$$

Sodium salt of Xylidin-azo-2-naphthol-3,6-disulpho acid.

Brownish red powder, readily soluble in water with yellowish red color.

The watery solution yields:

With muriatic acid, no change.

With liquor sodæ, darker and more yellowish colored.

In sulphuric acid, cherry-red solution; upon addition of water reddish yellow solution.

TEST IV.

Guinea pig (female). Age unknown, fully developed. Weight 0.403 ko. Was sullen and timid

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when received. Ate little; drank some milk. (May 16th.)

The color fed to the animal was dissolved in water in proportion of 1 gr. to 32 cc. of water. Each dose applied consisted of 4cc. of above solution. Through tube. The injections were made at 10 A. M., then the weight was taken and at 10.30 the animal received its food.

- May 17—Injection. Animal sullen. Weight 0.403 ko. Little appetite. Drank some milk.
- May 18-No injection. Animal less sullen. Weight 0.398 ko. Appetite increasing. Drinks milk with great desire.
- May 19th—Injection. Animal less sullen. Weight 0.400 ko. Appetite increasing. Hardly touches the milk.
- May 20th—No injection. Animal lively. Weight 0.402 ko. Good appetite.
- May 21st—Injection. Animal lively. Weight 0.403 Ko. Good appetite.
- May 22nd—No observatiou.
- May 23rd—Injection. Animal lively. Weight 0.402 ko. Considerable appetite.
- May 24—No injection. Animal less lively. Weight 0,404 ko. Less appetite. Drinks quite some milk.
- May 25th-Injection. Animal somewhat sullen and timid. Weight 0.400 ko. Eats little.
- May 26th—No injection. Animal quite lively. Weight 0.403 ko. Good appetite.

May 27th—Injection. Animal lively. Weight 0.404 ko. Good appetite.

May 28th—No injection. Animal lively. Weight scant 0.404 ko. Good desire to eat. No appreciable change in total weight. Discontinued.

RHODAMIN B.*

$$(C_2H_5)_2N$$

$$O$$

$$N(C_2H_5)_2$$

$$CO.OH$$

Phtalein of Diathylmetamidophenol (basic chlorhydrate).

Reddish to reddish-violet powder, soluble in water with bluish red color, diluted solutions of bluish pink color, fluoresce brownish. Readily soluble in alcohol with color same as watery solution, same fluorescence. Fluorescence disappears upon heating, reappears when cooled off.

The aqueous solution yields:

With muriatic acid, gradual precipitation of green crystals of the chlorhydrate; continued

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addition of muriatic acid produces scarlet color turning bluish red upon addition of water.

With liquor sodæ, if in small proportion, no change in the cold solution; if heated, precipitation of pink flakes. Addition of large proportion of liquor sodæ produces in the cold solution a precipitation of pink flakes, which are soluble in ether and benzol without color. When heated with liquor sodæ odor of dimethylamine.

In sulphuric acid, yellowish brown solution with production of muriatic acid. Solution fluoresces strongly greenish. Upon addition of water, the color of the solution changes first to scarlet and gradually to bluish red.

TEST V.

Very young rabbit (female) of 0.236 ko.

Animal was lively when received, seemed in good condition, displayed but little appetite. (May 16th.)

The color fed to the animal was dissolved in water in the proportion of 1 gr. to 25 cc. water. Each injection consisted of 2 cc. of solution with a little peptone through tube. The animal received one injection every other day at 10 A. M. Then the weight was ascertained and at 10.30 A. M. the animal received its fcod.

The test covered the period from May 17th to May 28th inclusive, when the test was discontinued.

During the whole period the animal seemed to be perfectly at ease, was lively, displayed good appetite and gained steadily, so that it would be superfluous to record each single day. The weight of the animal

on May 28th was 0.253 ko. or a total gain of 17 gr. The test was then discontinued.

NAPHTHOL YELLOW S.*

Potassium of sodium salt of 2.4-Dinitro-1-naphtol-7-sulpho acid.

Yellow or orange yellow powder, burns with yellow color, discharging at the same time sparks. Readily soluble in water with yellow color.

The aqueous solution yields:

With muriatic acid, no precipitate, solution becomes considerably lighter in color, eventually fades out entirely.

With KOH, even in very weak solutions, flaky precipitate.

With liquor sodæ, no change.

In sulphuric acid yellow solution; upon addition of water becomes lighter, but no precipitate.

TEST VI.

Male dog of 5.602 Ko. About two months old (?). Same dog as used in Test I.

When test commenced dog was lively, good appetite, drank normally, fæces normal.

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The color fed to the dog was dissolved in water in proportion of 1 gr. to 20 cc. water. The dose applied consisted of 4 cc. of above solution with a little peptone. Through tube.

The dog received the above dose every other day commencing June 1st and terminating June 14th. During the whole period the dog was uniformly lively and playful. The animal did not seem to dislike the color at all, but was always ready to receive the color without any attempt to avoid same. The appetite remained about uniformly good. The dog drank much milk and at the end of the test was in excellent condition. The weight taken daily showed a steady increase of from 2 to 6 gr. Weight on June 14th 5.661 gr. or a total increase of 59 gr. The test was then discontinued. The earlier part of July the dog was still in excellent condition and had gained considerably.

$$C_2H_5$$
 C_2H_5
 C_2H_5
 C_2H_5
 C_4
 C_6H_4
 C_6H_4
 C_8H_4
 C_8H

Sodium salt of diathyl-dibenzyldiamidotriphenylcar-binoltrisulpho acid.

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Green powder soluble in water with green color. Soluble in alcohol.

Aqueous solution yields:

With muriatic acid, yellowish brown color.

With liquor sodæ, discoloration and dirty violet clouding.

With barium chloride, no precipitate.

With picric acid, no precipitate.

In sulphuric acid, yellow solution which turns gradually green upon addition of water.

TEST VII.

Male guinea pig, fully developed, age unknown.

Animal seemed in excellent condition when test began. Same animal as used in Test III. Displayed good appetite before test commenced. Weight 0.521 ko. (May 31st.)

The color fed to this animal was dissolved in proportion of 1 gr. in 32 cc. water. Each injection consisted of 4cc. of above solution. Through tube. Injections were made at 10 A. M., then the weight was taken and at 10:30 A. M. the animal received its food. The animal received injection as described every other day commencing with June 1st and intended to cover the period of two weeks, but unfortunately on June 10th the animal met with an accident by falling out of its cage and had to be killed.

During the period in which the tests were made, that is, from June 1st to June 10th, the animal kept very lively and in good spirits. Had always considerable desire to eat, in fact, at times the appetite

seemed enormous for the size of the animal. Drank little milk twice a day, but not in excess. The weight continually varied between 0.521 and 0.519 ko. The last time the animal was weighed it showed 0.520 ko. As there was absolutely nothing irregular or abnormal observed during the whole test, there is no need of reporting or of specifying the result of each day.

Soluble Blue.*

• (Wasserblau.)

$$\begin{array}{c} CH_{3} \\ NH \cdot C_{6}H_{4}SO_{3}Na \end{array}$$

$$\begin{array}{c} NH \cdot C_{6}H_{4}SO_{3}Na \end{array}$$

$$\begin{array}{c} NH \cdot C_{6}H_{4}SO_{3} \end{array}$$

Sodium salts, ammonium salts, or calcium salts of triphenylrosanilin-and tryphenyl pararosanilintrisulpho acids.

Blue shining powder, soluble in water with blue color, but very little soluble in alcohol,

Aqueous solution yields:-

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With muriatic acid, no change in color. Partly blue precipitate.

With liquor sodæ, brownish red solution.

In sulphuric acid, dark reddish yellow. Upon addition of water blue solution and blue precipitate.

TEST VIII.

Guinea pig (female), age unknown but fully developed. Weight before test commenced 0.405 ko.

Animal lively. Good desire to eat. Animal seems in very good condition. Same animal as used in Test IV.

The soluble blue fed to the animal was dissolved in water in proportion of 1 gr. to 32 cc. water. Of this solution 4 cc. were uniformly taken as a dose, which was applied every other day through tube. Injections, as usual, were made at 10 A. M., then the weight was taken, and at 10:30 A. M. the animal received its food.

The test commenced on June 1st (first application of color), the last application was made on June 13th, and the last observation taken June 14th. Throughout this time the animal appeared to be in good health, was lively and possessed considerable appetite, especially was always desirous of drinking milk. Nothing irregular or disturbing whatsoever was observed during the whole period. The animal seemed to be perfectly at ease and no change of any account was to be noted. The weight gradually rose to 0.408 ko., this being the weight taken on June 14th, when the observation was discontinued.

NAPHTHOL RED S. *

$$\begin{array}{c}
N = N \cdot C_{10} H_6 \cdot SO_3 Na \\
\downarrow OH \\
Na O_3 S
\end{array}$$

$$SO_3 Na$$

Sodium salt of Naphthion-acid-azo-2-naphtol-3-6-disulpho acid.

Reddish brown powder. Readily soluble in water with fuchsine red color. Very little soluble in alcohol.

Aqueous solution yields:—

With muriatic acid, no change.

With liquor sodæ, solution becomes darker.

In sulphuric acid, violet solution; upon addition of water bluish violet.

TEST IX.

Very young male rabbit. Same animal as used in Test II.

Animal was in good condition when the test commenced. Appetite fair. Weight 0.282 ko.

The color fed to the rabbit was dissolved in water in proportion of 1 gr. in 25 cc. water. The dose applied consisted of 2 cc. of above solution with a little peptone. The injections were made at 10 A. M., through tube, then the weight was ascertained and at 10:30 A. M. the animal received its food.

^{*}G. Schultz & P. Julius Tabellarische Uebersicht.

June 1st—Injection. Animal lively. Weight 0.283 ko. Good appetite.

June 2nd—No injection. Animal less lively. Weight 0.281 ko. Appetite decreased.

June 3rd—Injection. Weight 0.279 ko. Otherwise same as on June 2d.

June 4th—No injection. Animal livelier. Weight 0.282 ko. Appetite increasing.

June 5th—No observation.

June 6th—Injection. Animal lively. Weight 0.281 ko. Considerable appetite.

June 7th—No injection. Animal lively. Weight 0.283 ko. Appetite good.

June 8th—Injection. Animal lively. Weight 0.286 ko. Appetite as usual.

June 9th—No injection. Animal lively. Weight 0.285 ko. Appetite good.

June 10th—Injection. Animal lively. Weight 0.287 ko. Appetite good.

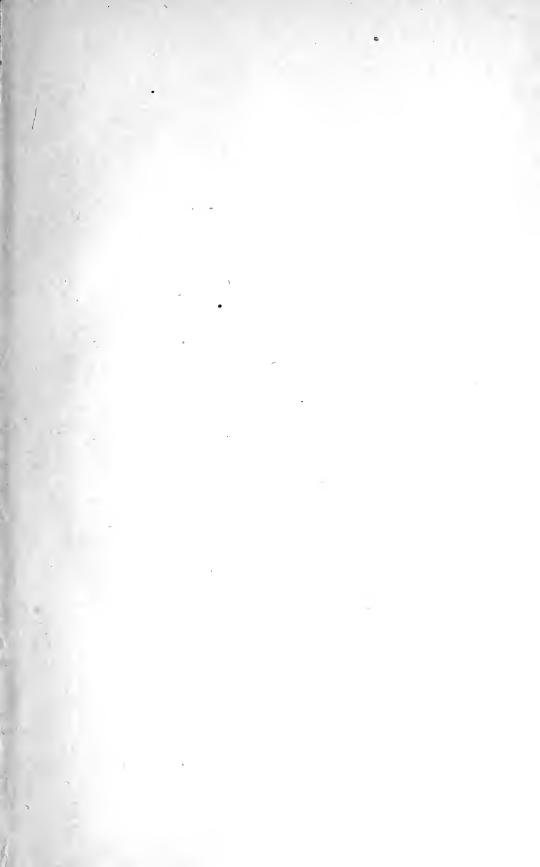
June 11th—No injection. Animal lively. Weight 0.289 ko. Appetite good.

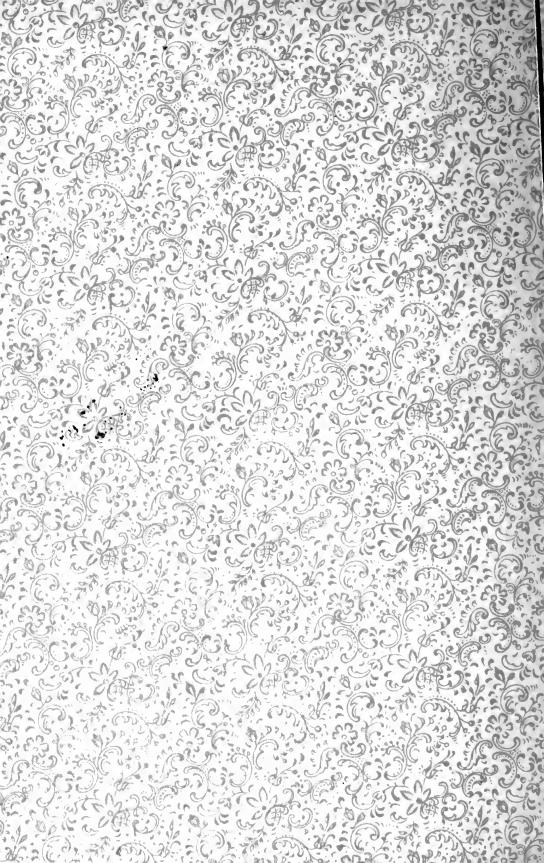
After feeding the animal in the afternoon it was caught between the doors of the cage when closing same, and as the animal seemed to suffer much pain it was killed. During the duration of the test the animal seemed perfectly at ease and gained 7 gr. in total weight. The apparent indisposition of the first days was of no great consequence.

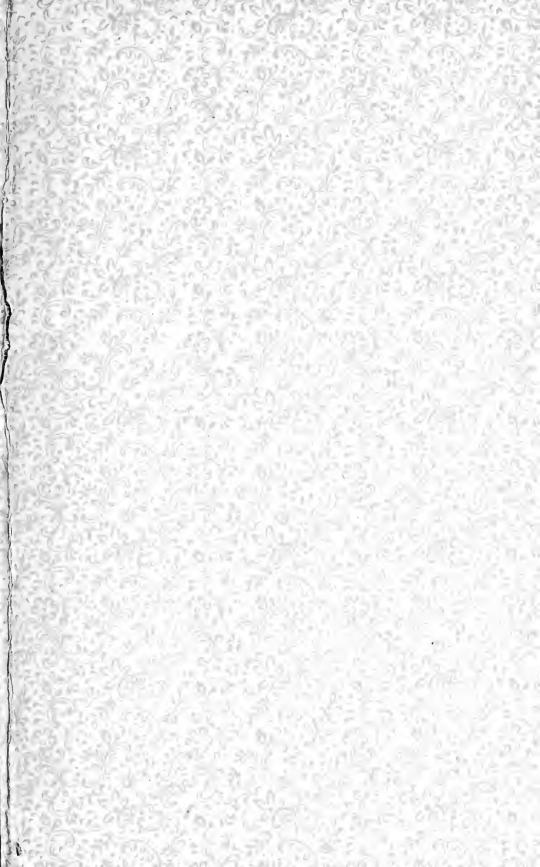
Owing to the number of coal tar colors already in existence and especially also considering the fact that their number increases very rapidly by new inventions, etc., it would be almost impossible to subject

everyone of them to similar tests, But this is, according to my opinion, not at all necessary, as by far the greatest number of these colors are never used for coloring of food products, but are solely employed for dyeing purposes in the various industries. it would be possible to draw quite reliable conclusions as to the advisability of employing certain colors for food products on the basis of their chemical constituency, the mode of their manufacture and of the ingredients used in same, nevertheless I think that the by far safest way would be on the one side to force the dealers of colors intended for food products to sell only such colors, with which exhaustive and careful physiological tests have been made by experienced and especially impartial and thoroughly reliable people, thereby establishing their harmlessness beyond a doubt. On the other hand the manufacturers and canners of food products of any description should be forced to purchase and use only such colors of which they are sure that they have been submitted to such careful tests as described before and through same have been found to be harmless.









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